P143922.PDF [Page: 2 of 81]

94-04681

National Défense
Defence nationale

NOVEL ACTIVATED CARBON IMPREGNANTS CONSISTING OF TRANSITION METAL COMPLEXES. PART I: BACKGROUND, SYNTHESES AND CHARACTERIZATIONS (U)

by

S.H.C. Liang, J.M. Whalen[1], R.L. Cooperstock[2] and B.O. Patrick[3]

Chemical Protection Section
Protective Sciences Division

[1] Defence Research Assistant, Summer 1990
[2] Defence Research Assistant, Summer 1992
[3] Co-op Student, Summer 1991

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
REPORT NO. 1197

PCN
0511B

December 1993
Ottawa

P143922.PDF [Page: 3 of 81]

ABSTRACT

In the search for novel impregnants for activated carbon to enhance its chemical activity, a variety of organometallic complexes containing transition metals which may be used as impregnants have been synthesized. Copper, chromium, cobalt and silver are the transition metals employed. The ligands studied included triethylenediamine (TEDA), quinuclidine (QUIN), acetylacetonate (acac) and its fluoro-derivative, hexafluoro-acetylacetonate (hfac), and some cyclic dienes such as 1,5-cyclooctadiene (1,5-COD). In all, three classes of organometallic complexes were studied. The first class consisted of metal salts using TEDA (or QUIN) as ligands. The second class consisted of transition metals using acetylacetone, and TEDA (or QUIN) as ligands. The last class consisted of transition metals, using acetylacetonate and cyclic dienes as ligands. In this report, the synthetic routes and the characterization of these organometallic complexes obtained by various spectroscopic techniques are detailed.

RÉSUMÉ

Dans le cours d'une recherche d'imprégnant originaux pour le charbon de bois activé et d'accroître ses activitées chimiques, une variété de complexes organométalliques contenant des métaux de transition qui peuvent être utilisés comme imprégnants ont été syntétisés. Les métaux de transition utilisés sont le cuivre le chrome, le cobalt et l'argent. L'étude des ligands inclait le triethylenediamine (TEDA), quinuclidine (QUIN), acétylacetonate (acac) et ses dérivés fluorés, l'hexafluoroacetylacetonate (hfac), et quelques dienes cycliques tel que le 1,5-cyclooctadienne (1,5-COD). En tout, trois classes de complexes organométalliques furent étudiés. La première classe comprenait des sels de métaux utilisant le TEDA (ou le QUIN) comme ligands. La seconde classe comprenait des métaux de transition utilisant l'acétylacétonate et le TEDA (ou QUIN) comme ligands. La dernière classe comprenait des méaux de transition, utilisant l'acetylacetonate et des dienis cycliques comme ligands. Ce rapport énumère en détail les routes syntétiques et les charactéristiques de ces complexes organométalliques obtenus par différentes techniques spectroscopiques.

EXECUTIVE SUMMARY

The activated carbon currently used in respiratory and collective protection equipment is impregnated with copper, chromium, silver and triethylenediamine (TEDA) to enhance its chemical activity. In an effort to enhance the chemical activity further, an attempt has been made to utilize organometallic complexes containing transition metals as a replacement impregnant for activated carbon. Three classes of organometallic complexes are investigated in this study using copper, chromium, cobalt and silver as the coordinating metal atoms. The first class consisted of complexes formed between metal salts and ligands such as triethylenediamine (TEDA) or quinuclidine (QUIN). The second class consisted of complexes containing the transition metals, acetylacetonate (and its fluoro-derivative, hexafluoro-acetylacetonate), and TEDA (or QUIN) as ligands. The third class consisted of the transition metal hexafluoroacetylacetonates, and some selected cyclic dienes as ligands. In this report, the first part of a two-part study on the choice of organometallic complexes as novel impregnants on the activated carbon surface, the synthetic routes and the characterization of these organometallic complexes are discussed.

TABLE OF CONTENTS

Page

ABSTRACT/RÉSUMÉ iii

EXECUTIVE SUMMARY v

LIST OF FIGURES ix

1.0 INTRODUCTION 1

1.1 DEFINITION OF THE PROBLEM 2
1.2 APPROACH TO THE PROBLEM 3

2.0 LITERATURE REVIEW ON ORGANOMETALLIC COMPLEXES CONTAINING TRANSITION METALS 4

2.1 AMINE-TRANSITION METAL COMPLEXES 5

2.1.1 Steric and Electronic Effects 5
2.1.2 Basicity of the Amines 5
2.1.3 Cyclic vs Aliphatic Amines 6
2.1.4 Quaternary Amines 7

2.2 TRANSITION METAL COMPLEXES CONTAINING AMINE LIGANDS AND PENTANE-2,4-DIONE AND ITS DERIVATIVES 9
2.3 OTHER ORGANOMETALLIC COMPLEXES CONTAINING TRANSITION METALS 11

3.0 MATERIALS AND EQUIPMENT 13

3.1 STARTING MATERIALS PROCURED FROM COMMERCIAL SOURCES 13
3.2 CHEMICALS SYNTHESIZED AT DREO 16
3.3 FOURIER TRANSFORM INFRARED (FTIR) MEASUREMENTS . . 17
3.4 NUCLEAR MAGNETIC RESONANCE (NMR) MEASUREMENTS . . . 17
3.5 UV/VIS MEASUREMENTS 17

4.0 SYNTHETIC PROCEDURES FOR THE TRANSITION METAL COMPLEXES 17

4.1 PREPARATION OF SOME PRECURSOR COMPOUNDS 17

4.1.1 $Cu(laurate)_2$ 18
4.1.2 $Cu(acac)_2$ 18
4.1.3 $Cu(dmg)_2$ 18

P143922.PDF [Page: 6 of 81]

Page

4.2 TYPICAL SYNTHETIC PROCEDURES 18

4.2.1 Preparative Procedure "A" 19
4.2.2 Preparative Procedure "B" 19
4.2.3 Preparative Procedure "C" 19

4.3 GENERAL SCHEMES OF PREPARATIONS AND CHARACTERIZATIONS 20

5.0 DISCUSSIONS 20

5.1 PREPARATIONS AND PHYSICAL DATA OF METAL SALTS AND TEDA/QUIN COMPLEXES 20

5.1.1 Copper Complexes 25
5.1.2 Chromium Complexes 26
5.1.3 Silver Complexes 26

5.2 PREPARATIONS AND PHYSICAL DATA OF METAL ACETYLACETONATES AND TEDA/QUIN COMPLEXES 27

5.2.1 Copper Complexes 27
5.2.2 Cobalt Complexes 28
5.2.3 Chromium Complexes 28

5.3 PREPARATIONS AND PHYSICAL DATA OF OTHER COMPLEXES 28

5.3.1 Copper Complexes 28
5.3.2 Cobalt Complexes 30
5.3.3 Silver Complexes 30

6.0 CONCLUSIONS 30

7.0 REFERENCES 31

LIST OF FIGURES

Figure 1: FTIR spectrum of $Cr(acac)_3$ in nujol.

Figure 2: FTIR spectrum of $Co(acac)_3$ in nujol.

Figure 3: FTIR spectrum of $Co(acac)_2 \cdot H_2O$ in nujol.

Figure 4: FTIR spectrum of $Co(hfac)_2 \cdot H_2O$ in nujol.

Figure 5: FTIR spectrum of $CuCl_2$ in nujol.

Figure 6: FTIR spectrum of $Cu(hfac)_2 \cdot H_2O$ in nujol.

Figure 7: UV/VIS spectrum of $Cu(hfac)_2 \cdot H_2O$ in $CHCl_3$ from 240 to 400 nm (2×10^{-5} M).

Figure 8: UV/VIS spectrum of $Cu(hfac)_2 \cdot H_2O$ in $CHCl_3$ from 600 to 820 nm (2.1×10^{-2} M).

Figure 9: FTIR spectrum of triethylenediamine in nujol.

Figure 10: FTIR spectrum of quinuclidine in nujol.

Figure 11: FTIR spectrum of $Cu(acac)_2$ in nujol.

Figure 12: FTIR spectrum of bis(dimethylglyoximato)copper(II), $Cu(dmg)_2$ in nujol on ZnSe plates.

Figure 13: UV/VIS spectrum of $Cu(dmg)_2$ in ethanol (7×10^{-5} M).

Figure 14: FTIR spectrum of $Cu(laurate)_2$ in nujol.

Figure 15: FTIR spectrum of $CuCl_2 \cdot$ (TEDA) in nujol.

Figure 16: FTIR spectrum of $CuCl_2 \cdot$ (QUIN) in nujol.

Figure 17: FTIR spectrum of $Cu(laurate)_2 \cdot \frac{1}{2}$(TEDA) in nujol.

Figure 18: FTIR spectrum of $Cu(laurate)_2 \cdot x$(QUIN) in nujol.

Figure 19: FTIR spectrum of $Cu(acetate)_2 \cdot \frac{1}{2}$(TEDA) in nujol.

Figure 20: UV/VIS spectrum of $Cu(acetate)_2 \cdot \frac{1}{2}$(TEDA) in methanol ($1 \times 10^{-4}$ M)

Figure 21: FTIR spectrum of $Cr(NO_3)_3 \cdot x$(TEDA) in nujol.

Figure 22: FTIR spectrum of $Cr(NO_3)_2 \cdot x$(QUIN) in nujol.

Figure 23: FTIR spectrum of $AgNO_3 \cdot x$(TEDA) in nujol.

Figure 24: FTIR spectrum of $Cu(hfac)_2 \cdot (TEDA)$ in nujol.

Figure 25: UV/VIS spectrum of $Cu(hfac)_2 \cdot (TEDA)$ in CCl_4 (1.7×10^{-4} M) from 320 to 520 nm.

Figure 26: UV/VIS spectrum of $Cu(hfac)_2 \cdot (TEDA)$ in CCl_4 (1.7×10^{-2} M) from 600 to 800 nm.

Figure 27: FTIR spectrum of $Cu(acac)_2 \cdot x(QUIN)$ in nujol.

Figure 28: FTIR spectrum of $Co(acac)_2 \cdot x(TEDA)$ in nujol.

Figure 29: FTIR spectrum of $Co(acac)_2 \cdot (QUIN)$ in nujol.

Figure 30: FTIR spectrum of $Co(hfac)_2 \cdot 2(TEDA)$ in nujol.

Figure 31: FTIR spectrum of $Cu(hfac) \cdot (1,5\text{-COD})$ in nujol.

Figure 32: ^1H NMR spectrum of $Cu(hfac) \cdot (1,5\text{-COD})$ in THF-d_8.

Figure 33: FTIR spectrum of $Cu(dmg)_2 \cdot (TEDA)$ in nujol.

Figure 34: UV/VIS spectrum of $Cu(dmg)_2 \cdot (TEDA)$ in ethanol (2.9×10^{-4} M).

Figure 35: FTIR spectrum of $Ag(hfac) \cdot (1,5\text{-COD})$ in nujol.

Figure 36: ^1H NMR spectrum of $Ag(hfac) \cdot (1,5\text{-COD})$ in $CDCl_3$.

Figure 37: FTIR spectrum of $Ag(hfac) \cdot (1,4\text{-CHD})$ in nujol.

Figure 38: ^1H NMR spectrum of $Ag(hfac) \cdot (1,4\text{-CHD})$ in DMSO-d_6.

1.0 INTRODUCTION

One of the projects in the respiratory protection program within Defence Research Establishment Ottawa (DREO) is to improve the performance of the current adsorbent, the impregnated activated carbon employed in respirator canisters. ASC Whetlerite, an activated carbon impregnated with copper, chromium and silver, and its derivative ASC/T, an ASC carbon further impregnated with triethylenediamine (TEDA) are the current adsorbents of choice for military air filters in Canada. This formulation of impregnants consisting of copper, chromium and silver was developed 50 years ago and has been extensively used ever since (1). At the optimum concentration of 6-8% copper, 2% chromium, 0.05% silver and 2% TEDA, the ASC/T carbon is optimized for protection against toxic gases such as hydrogen cyanide (AC), cyanogen chloride (CK), phosgene (CG), mustards and nerve agents. However there are several drawbacks associated with the ASC and ASC/T carbon, such as short service life (i.e. susceptibility to ageing and weathering) and poor performance at high relative humidity. Combinations of copper with other metals such as vanadium, molybdenum and manganese, etc. have been attempted as impregnants without too much success (1,2). The failures are either due to an impregnated carbon of an inferior quality (i.e. with lower protection against toxic gases), or to the fact that the impregnated carbon is more difficult to produce. Organic compounds, such as tartaric acid and various amines (TEDA was one of the most successful candidate amines) have also been used as co-impregnants to enhance protection against CK and AC, and to prolong the service life of the impregnated carbon.

DREO has been engaged in projects to enhance the performance of the activated carbon in two ways: (i) to understand the chemical and physical relationships at the carbon surface between the impregnants and the toxic gases so that suitable changes in the impregnants (composition, etc.) can be made; and (ii) to elucidate the changes in the metal impregnants upon ageing, so that suitable modifications can be made to the carbon surface or the impregnant to stop or to slow down the performance loss due to ageing.

It has been pointed out earlier that various combinations of copper and other metals have been used as impregnants. Thus the choice of alternate impregnants is restricted to promising new combinations only. This report and a subsequent one, will detail the work carried out at DREO since 1989 in using transition metal complexes as alternate impregnants on activated carbon. This report will detail the background, the synthetic routes and the characterization of some of these transition metal complexes. Further work will focus on how these transition metal complexes are impregnated onto activated carbon and their performance against selected toxic gases. The following two sections (Sections 1.1 and 1.2) introduce the problem at hand, that is, the search for new

impregnants, and the approach adopted by DREO in solving this problem. These two sections will delineate the following key points:

(i) the nature of the chemical impregnants and active species which exist on the ASC carbon surface, and how they are perceived as organometallic complexes containing triethylenediamine and copper, silver or chromium;

(ii) the premise of the hypothesis made above, and how it can be tested.

1.1 DEFINITION OF THE PROBLEM

The choice of transition metal complexes or more specifically, organometallic complexes as novel impregnants on activated carbon is by no means accidental. Currently, the three inorganic components in the Whetlerization formula are copper, chromium and silver - all are transition metals and all are capable of forming stable organometallic complexes (3). The organic component of the impregnation formulation consists of triethylenediamine, a bicyclic diamine. It is well known that amine compounds can form stable ligands, and that di-amines form stable chelates (i.e. bi-dentate ligands) to a central transition metal atom (3). Since the lower energy d-orbitals on the nitrogen atom are at too high an energy level to use, ligands containing amine compounds are usually the classical or simple donor ligand type. This type of ligand requires the central metals to be Lewis acids (or metal ions); thus almost all organometallic complexes containing amine compounds consist of a central metal atom which is charged. Although the TEDA molecule contains two nitrogen atoms (2 electron pairs, or a four electron donor), it cannot form a chelate because the two electron pairs are facing away from each other. Thus, TEDA molecules are expected to form unidentate ligands with central metal ions. It is obvious that ASC/T carbon contains ingredients, which by themselves can be made into transition metal complexes. Furthermore, these impregnants, when placed on the carbon surface, may exist as transition metal complexes on the carbon surface and may be responsible for all its chemical reactions with the toxic gases. This is the basis for DREO's interest in using transition metal complexes as impregnants on the activated carbon surface.

The nature of the active species on ASC/T carbon was never clear. It was never certain where the adsorption sites for TEDA are: close to the metal ions, or at other distinct sites distant from metal ions. However, unless the copper and chromium exist together as molecular species such as copper chromate, copper chromite, or even as $CuOHNH_4CrO_4$, as proposed by Hammarstrom and Sacco (4), there is a great tendency for TEDA to be attached to the copper and chromium ions because of electrostatic interaction

between the lone pair of electrons on TEDA and the metal cations. In such a case, one can postulate a ligand formation between the TEDA molecule and the metal ions on the carbon surface, similar to those observed for organometallic complex type compounds. Thus the employment of $Cu(TEDA)_x$ or $Cr(TEDA)_x$ (x = 1 to 3) type complexes as carbon impregnants may provide insight into 2 questions:

(i) What is the nature of the impregnants on the surface of the ASC/T carbon?

(ii) How well will organometallic complexes consisting of transition metals perform as impregnants on the activated carbon surface?

The answers to these two questions could only be obtained from the performance study of these impregnated carbons, i.e. the protection against toxic gases and vapors afforded by these impregnated carbons. This subject will be elaborated in detail in a future report.

1.2 APPROACH TO THE PROBLEM

In order to assess the effectiveness of transition metal complexes as impregnants on activated carbon, the following points should be considered:

(i) Synthesis: The first priority is to determine if the desired transition metal complexes can be synthesized, or if the synthetic routes to them are too complicated. Attention should be directed to this problem first.

(ii) Impregnation: Loading transition metal complexes onto the activated carbon may pose a problem. In the Whetlerization process, all the metal impregnants are loaded onto the carbon from an aqueous phase. Most organometallic complexes are insoluble in water; thus, another solvent may have to be used. However, it has been observed in some cases (e.g. in the impregnation of hexachloroplatinic acid on carbon) that the adsorption is less strong when a non-aqueous solvent is used (5). This suggests that the resulting impregnated carbon may not be as effective because the impregnants are less strongly held to the surface. It should be noted that the chemistry of the impregnation process and the activated carbon surface are still not well understood.

(iii) Reactivity: It is well known that many organometallic complexes containing transition metals such as platinum, rhodium and ruthenium are good homogeneous catalysts in oxidation-reduction (including hydrogenation), and isomerization reactions, etc. Furthermore, supported

catalysts on various surfaces containing metals and organometallic complexes have been extensively studied (6) particularly on carbon surfaces, both activated carbon and carbon black (6b, 6c). Although the synthetic route to these catalysts is laborious, they are all reactive.

It is apparent from the above points that transition metal complexes may be good candidates as alternate impregnants for activated carbon for chemical activity enhancement. However, to study this in a systematic way, the following step-by-step experimental approach was undertaken. First, it has been determined that the logical place to start is to prepare complexes containing TEDA and some transition metals, e.g. copper, chromium, etc. A literature review was performed on this subject. It was determined that TEDA complexes can be prepared by mixing salts of transition metals (e.g. halide salts of copper, cobalt, manganese and zinc, etc.) with triethylenediamine. However, it was also discovered that most of these organometallic complexes are insoluble in most solvents, making them unsuitable as impregnants. The second step was to synthesize other types of transition metal-TEDA complexes. A literature review showed that the complex, bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-copper(II) ($Cu(hfac)_2$) reacts with TEDA to form a $Cu(hfac)_2(TEDA)$ complex, which is soluble in chloroform and tetrahydrofuran, making $Cu(hfac)_2(TEDA)$ a good candidate impregnant. From this information, complexes containing other transition metals and the hexafluoroacetylacetone and triethylenediamine ligands were prepared as possible candidate impregnants on activated carbon. The third step followed directly from the results obtained in the second step. If $Cu(hfac)_2(TEDA)$ type complexes can be made and employed as impregnants, Cu(acac) (where acac ≡ pentane-2,4-dione, the non-fluorinated derivative of hfac) and other $Cu(acac)_2(L)$ (L≡ligand such as cyclic dienes) or $Cu(hfac)_2(L)$ type complexes could be prepared and assessed as impregnants on activated carbon.

2.0 LITERATURE REVIEW ON ORGANOMETALLIC COMPLEXES CONTAINING TRANSITION METALS

This literature review focussed on transition metal complexes which can be used as impregnants on activated carbon. Thus, emphasis is placed first, on transition metals such as copper, chromium and silver which are the three transition metals currently used as impregnants; and secondly, on ligands such as triethylenediamine (TEDA) which is the active organic impregnant. This review consists of three sections. Section 2.1 will briefly describe transition metal complexes containing amines, especially TEDA. Section 2.2 discusses another way to synthesize transition metal complexes containing TEDA using a complex such as bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)copper(II) as the starting material. Section 2.3 will describe other transition

metal complexes which can be employed as activated carbon impregnants, drawing on the experience gained in Section 2.2.

2.1 AMINE-TRANSITION METAL COMPLEXES

There are many known transition metal complexes containing amines, both aliphatic and cyclic (7-25). In particular, extensive research has been devoted to complexes containing triethylenediamine (TEDA) and quinuclidine (QUIN), and their aliphatic analogues, N,N,N',N'-tetramethylethylenediamine (TMEN) and triethylamine (TEA) respectively. The majority of the references employed first row transition elements with an emphasis on copper and cobalt (7, 9-10, 12-16, 18-19, 23). Different forms of the complexes have been synthesized, with differing coordination numbers, geometries, etc., as evidenced by spectrophotometric and X-ray analyses.

2.1.1 Steric and Electronic Effects

A study of the different complexes that can be formed with quinuclidine, triethylamine, triethylenediamine and tetramethylethylenediamine gives insight as to the importance of steric effects (bicyclic versus aliphatic amines, both tertiary) as well as the identity of atoms at key positions (C versus N), i.e., electron inductive effects etc. (7-25). For example, a comparison of quinuclidine and triethylenediamine revealed the following information: when an excess of quinuclidine was mixed with $CuCl_2$, an orange brown solid consisting of $CuCl_2 \cdot$ (QUIN) was obtained (10). When an excess of triethylenediamine was mixed with $CuCl_2$, a brown solid, $CuCl_2 \cdot \frac{1}{2}$(TEDA) was formed. In similar experiments, where $CoCl_2$ was used, a deep blue compound, $CoCl_2 \cdot 2$(QUIN) was readily obtained, while no definite product corresponding to $CoCl_2 \cdot x$(TEDA) could be produced (10). In other experiments using $AgNO_3$, the compounds $AgNO_3 \cdot 2$(QUIN) and $AgNO_3 \cdot 1.5$(TEDA) were obtained (8). In another study where copper(II) (acetate) was used, two light green precipitates corresponding to $Cu(acetate)_2 \cdot$(QUIN) (ratio of amine to copper was slightly greater than 1:1) and $Cu(acetate)_2 \cdot \frac{1}{2}$(TEDA) (ratio of amine to copper was slightly less than 0.5:1) were obtained (9). The same study also demonstrated that both quinuclidine and triethylenediamine have lower steric hindrance than triethylamine because similar compounds were not formed when triethylamine was reacted with copper acetate.

2.1.2 Basicity of the Amines

In the triethylenediamine molecule, the two nitrogen atoms are close to each other, and do interact, as reported by Quagliano et al (14). It was also shown that the first pK_a of this compound

is 8.60, significantly lower than the value of 10.65 for quinuclidine. Furthermore, monoprotonated and monomethylated triethylenediamine are less basic than triethylenediamine itself. Electron spin resonance (ESR) studies revealed that the environment of the two nitrogen atoms is equivalent (14). Another study by Rudzinski et al (20) has shown that these two nitrogen atoms have widely different basicities (pK_{a1} = 8.19 and pK_{a2} = 4.18). It was therefore expected that triethylenediamine would behave as a monodentate ligand. This was demonstrated in a study of the reaction between bis(O,O'-diethyldithiophosphato)nickel(II) and triethylenediamine, by the fact that two molecules of bis(O,O'-diethyldithiophosphato) nickel(II) coordinated to one molecule of triethylenediamine (20). It seems that the formation of a bridged adduct is not precluded by the low basicity of the second nitrogen atom. The basicity of the second nitrogen atom in triethylenediamine "is probably decreased by through-bond inductive interactions rather than by through-space interactions" (20). This decrease in basicity, however, is less than that expected if the first nitrogen atom in triethylenediamine is protonated (20).

2.1.3 Cyclic vs Aliphatic Amines

There are several reports (8-10) comparing bicyclic nitrogen containing compounds with their linear analogues as ligands to transition metal elements. A good example is illustrated by the bis(TMEN) complexes (TMEN=N,N,N',N'-tetramethylethylenediamine, is a linear analogue of triethylenediamine) versus bis(TEDA) complexes with the first row transition metal element prepared in aqueous solution (8-10). $CuCl_2$ and tetramethylethylenediamine form a 1:1 complex, while $CoCl_2$ and tetramethylethylenediamine form two types of compounds, a stable blue 1:1 tetrahedral complex, as well as an unstable pink, six-coordinated complex (10). However, not all the structure or geometry of these compounds is well understood, e.g. the bis(TMEN)zinc compound (24) or the two complexes involving nickel: $[Ni(TMEN)_2(ClO_4)_2]$ and $[Ni(TMEN)_2(CH_3CN)_2]ClO_4)_2$ (25). In the case of the nickel compound, it is not known whether the diamine units are chelating or bridging. It is important to note that the steric interference of the N-methyl substituents on the ligand is important but does not rule out the formation of bis(TMEN) complex.

It should be pointed out that it is unreasonable to compare tetramethylethylenediamine with triethylenediamine as ligands since the former acts as a chelating agent, while the latter is non chelating. However, comparisons can be drawn between quinuclidine and its non bicyclic analogue, triethylamine. Two things would be expected: first, an equal or greater number of quinuclidine molecules than triethylamine molecules are expected to coordinate to the central metal ion; and second, a stability advantage is expected for the quinuclidine complexes (10). When reactions involving $CoCl_2$ and the amines were carried out, two

pseudotetrahedral complexes $CoCl_2 \cdot 2(QUIN)$ and $CoCl_2 \cdot (TEA)$ were obtained (10). These ratios agreed with expected results. However, the converse holds when copper was used: $CuCl_2 \cdot (QUIN)$ and $CuCl_2 \cdot (TEA)$ were obtained, the latter being unstable above 0°C with respect to oxidation/reduction reactions (10). It seems that in the case of $CuCl_2 \cdot (QUIN)$, the amine apparently makes little contribution to the ligand field primarily due to the presence of the chloride ions in the polymeric solid structure. In a study of the silver(I) complexes of bicyclic tertiary amines, comparisons were made between quinuclidine and triethylenediamine, and their aliphatic analogues, tetramethylethylenediamine and triethylamine as ligands to $AgNO_3$ (8). The solid complexes $AgNO_3 \cdot 2(QUIN)$ and $AgNO_3 \cdot 1.5(TEDA)$ were formed as was described previously, and in addition, $AgNO_3 \cdot 2(TEA)$ (melting point = 0°C) and $AgNO_3 \cdot 2(TMEN)$ (melting point = 100°C) were also obtained. However, when DMSO (dimethylsulfoxide) was used as solvent for the reaction, only $AgNO_3 \cdot (TEA)$ was formed while the same complexes were obtained for the other three amines. This demonstrates the importance of steric interference between two triethylamine molecules in the presence of competing solvent molecules, DMSO (as ligands). A similar comparison between triethylenediamine and tetramethylethylenediamine (based on steric effects) is not valid, since these two differ in the ligand formation towards silver(I), i.e. chelate formation is involved in the $AgNO_3 \cdot 2(TMEN)$ complex, whereas chelation is impossible in the $AgNO_3 \cdot 1.5(TEDA)$. It can thus be concluded that nonchelating aliphatic tertiary amines are relatively weak ligands and that reduction of steric hindrance by placing the nitrogen atom at the bridgehead of a bicyclic system has a small effect on the formation constants, but a more obvious effect on the coordination number of silver ion toward the amine in the presence of competing ligands (8).

Another study comparing tertiary bicyclic nitrogen-containing compounds with their aliphatic analogues involves copper(II) acetate complexes in dimethylformamide (DMF) solvent. The compounds $Cu(acetate)_2 \cdot (DMF)$, $Cu(acetate)_2 \cdot (TMEN)$, $Cu(acetate)_2 \cdot \frac{1}{2}(TEDA)$ and $Cu(acetate)_2 \cdot (QUIN)$ were formed (9). However, $Cu(acetate)_2 \cdot (TMEN)$ was formed only when the ratio of tetramethylethylenediamine to copper exceeded 1:1. The lower steric requirement of quinuclidine compared to triethylamine is reflected in the formation of the complex $Cu(acetate)_2 \cdot (QUIN)$ in dimethylformamide solution while triethylamine was unable to displace the solvent (DMF) from the coordination sphere of copper(II). Both the bicyclic diamine TEDA and the open-chain diamine TMEN reacted with copper acetate in DMF to yield their respective complexes.

2.1.4 Quaternary Amines

A good deal of research (11, 14) has been devoted to monoquaternized (monoprotonated or monomethylated) and

diquaternized nitrogen containing ligands. This work was performed to study the donor properties of positively charged ligands. The total entropies of protonation for these compounds are positive due to a net release of water molecules during protonation (11). A comparison of the protonated forms of ethylenediamine, piperazine and triethylenediamine has been made. The mono-quaternized triethylenediamine cations would be expected to be poor ligands because the donor nitrogen atom is a tertiary nitrogen of very low basicity, and does not offer the possibility of π back-donation from the metal ions. However, "the rigidity and compact cage-like structure of protonated-TEDA ion effectively relieves the steric hindrance to coordination, which in tertiary aliphatic amines arises from the flexibility of the nitrogen bonded alkyl groups. Furthermore, the rigid, spherical shape of the triethylenediamine cation prevents any conformational isomerism which could lead to structural complications" (14). Instead, the shape of this ligand favours the formation of a regular and compact crystal lattice.

Various compounds with the formula $MX_2(L^*)X$ have been synthesized (14) by reacting metal halides (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II), X = Cl, Br and I, and L^* = triethylenediamine cation) with the corresponding halide of monoprotonated or monomethylated triethylenediamine. The X-ray powder patterns of the compounds have revealed isomorphous structures when M = Mn(II), Fe(II), Co(II), Ni(II), or Zn(II). The most important piece of information in terms of the stereochemistry of the metal ions, especially of Co(II) and Ni(II) is obtained from the d-d electronic absorption spectra (14). The triethylenediamine ion and the three halide ions are coordinated to the central metal ion, forming nonionic, mononuclear entities of the formula $[M(L^*)X_3]$. This is also the case with M = Mn(II), Fe(II) and Zn(II). The corresponding copper complex has a pseudotetrahedral stereochemistry but is not isomorphous with the Co(II) and Ni(II) complexes. However all these compounds are insoluble in most organic solvents (sparingly in nitromethane), and are decomposed by water and other strong donor solvents. The monoprotonated complexes are less soluble than the monomethylated ones, and the identity of the halide has an effect on the solubility. The solubility increases in the order: chloride complexes < bromide complexes < iodide complexes.

Additional work by Vallarino et al (16) on these mono-protonated ditertiary amines can be summarized as follows: (i) the positive charge on the ligand leads to strong electrostatic interactions, which increase the overall lattice energy and solid state stability of the complex; (ii) in contrast with aliphatic amines, the rigid structure of the triethylenediamine ion, for instance, minimizes the steric requirements necessary for coordination to metal ions; and (iii) the availability of the lone pair of electrons on the nitrogen donor atom may be reduced by direct electronic interaction with the monoquaternized positively charged nitrogen atom. Reactions between the chlorides and

bromides of Mn(II), Fe(II), Ni(II), and Cu(II) and an excess of the monoprotonated triethylenediamine halide form compounds of formula $MX_2 \cdot 2(L^+H)X$. These are crystalline solids which dissolve in solvents with good donor properties, such as water and DMSO. The Mn(II), Fe(II) and Ni(II) complexes have superimposable vibrational spectra, and based on X-ray powder patterns, these complexes are isomorphous. Two likely structural formulas corresponding to $NiX_2 \cdot 2(L^+H)X$ are given as $[NiX_3(L^+H)_2] \cdot X$ and $(L^+H) \cdot [NiX_4(L^+H)]$, both having trigonal bipyramidal structures. The corresponding Cu(II) - monoprotonated triethylenediamine complexes, however, are not isomorphous with those of Mn(II), Fe(II), and Ni(II), but probably have closely related structures. A five-coordinate, trigonal bipyramidal structure was proposed for $[CuX_3(L^+H)_2] \cdot X$. The infrared spectrum is the same as for the Ni(II), Fe(II) and Mn(II) complexes. The corresponding Co(II) and Zn(II) complexes were also described. They are four-coordinate, pseudotetrahedral zwitterionic complexes of the formula $[MX_3(L^+H)]$. All the $[MX_3(L^+H)_2] \cdot X$ complexes have high thermal stability (stable up to ~200°). Apparently, the network of hydrogen bonds formed through the N^+-H of the protonated TEDA cation ligands greatly contributes to the stabilization of the crystalline $[MX_3(L^+H)_2] \cdot X$ complexes. They decompose in the presence of atmospheric moisture, the bromide complexes being more sensitive than the chloride ones.

Several diprotonated triethylenediamine complexes have been synthesized (19). These are of the formula MX_4LH_2, where M = Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, or Mn^{2+}, and X = Cl or Br (21). They have a tetrahedral structure, and all are isomorphous.

2.2 TRANSITION METAL COMPLEXES CONTAINING AMINE LIGANDS AND PENTANE-2,4-DIONE AND ITS DERIVATIVES

The coordinative saturation of metal(II) acetylacetonates (acac, also called pentane-2,4-dionates) may be achieved through the addition of Lewis bases (26). Unidentate ligands lead, in general to axial attachment as in trans-bis(pentane-2,4-dionato)-bis(pyridine)cobalt(II), or -nickel(II) (27), although a cis-octahedral geometry has been reported for bis(pentane-2,4-dionato)-bis(pyridine-N-oxide)-nickel(II) (28). The cis-octahedral geometry has been observed for some bi-dentate, and chelating diamine ligands, such as bipyridine, as long as there is a progressive fluorine substitution on the methyl group. Progressive trifluoromethylation of the acetylacetone ligand has been shown to increase the affinity of the central metal atom for ligand attachment (15). It has been shown (15) that acetylacetonate (acac), trifluoroacetylacetonate (tfac) and hexafluoro-acetylacetonate (hfac or 1,1,1,5,5,5-hexafluoropentane-2,4-dionate) ligands react differently with TEDA. Reaction of bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)-copper(II) hydrate with equimolar amounts of TEDA yielded $Cu(hfac)_2 \cdot (TEDA)$, which is an acicular

yellow-green orthorhombic crystal with a trans-octahedral geometry. When the ratio of the reactants, $Cu(hfac)_2$ to TEDA is 1:2, the product $Cu(hfac)_2 \cdot (TEDA)_2$ is obtained. This compound is a garnet red crystal and the infrared spectrum showed a cis-octahedral geometry. Low-temperature nuclear magnetic resonance (NMR) studies of similar compounds, bis(4-picoline) adducts of bis(diketonato)-nickel complexes have also indicated the increasing amount of cis-isomers when trifluoroacetylacetonate and hexafluoroacetylacetonate replace acetylacetonate as the di-ketones (29). The reaction of $Cu(tfac)_2$ with TEDA gave only $Cu(tfac)_2 \cdot (TEDA)$, illustrating the effect of trifluoromethylation on coordinative saturation. For the reaction between $Cu(acac)_2$ and TEDA, no isolable products were obtained. The reaction between $Cu(hfac)_2$ and TEDA is most intriguing. Apart from the different products observed when the ratio of reactants varied, an attempt to make a protonated TEDA cation from $Cu(hfac)_2$ hydrate, hexafluoroacetylacetonate and TEDA in a 1:1:1 ratio gave $[Cu(hfac)_2]_2 \cdot (TEDA)$, whose composition was confirmed by X-ray diffraction.

The influence of fluorine substitution on the properties of copper(II) chelate compounds has been investigated (30). Based on ultraviolet (UV) spectroscopic studies, trifluoromethylation of acetylacetonate increases the wavelength and intensity of the maximum of the intense absorption band. This can be attributed to the electron attracting ability of the trifluoromethyl group which increases the amount of enolization; i.e. trifluoroacetylacetonate can exist in the following isomeric enol forms:

The maximum of the intense absorption band of hexafluoroacetyl-acetonate, however, is decreased in intensity and frequency compared to acetylacetonate. The wavelength shifts with fluorine substitution are what one would expect: an increase when a strong electron-attracting group is placed on one end of a conjugated system, and a decrease when such electron-attracting groups are placed on both ends of the system. Based on the absorption intensities, it is possible to estimate the percent enolization of the compounds in a given solvent. While these values are not precise, one can safely draw from them the conclusion that an increase in the electron-donating power of the alkyl groups next to the carbonyl carbon produces a corresponding increase in the intensity of K-absorption (30). The absorption spectra of the

copper(II) chelates in the visible region clearly indicate that the effect of substitution by trifluoromethyl groups in the ligand is to shift the absorption bands to longer wavelengths, thus passing more light in the low-wavelength region and accounting for the typically green colour of copper chelates of fluorinated ligands. This shift of the absorption bands increases as the number of trifluoromethyl groups increases, and thus correlates with a decrease in the stability of the metal chelate (30).

The infrared spectra show a shift of the OH stretching vibration, corresponding to the enolized form, from 3550cm^{-1} for acetylacetonate to 3360cm^{-1} for trifluoroacetylacetonate, indicating that the enol of the latter is more acidic than that of the former. The pK_a value of hexafluoroacetylacetonate obtained from titration is approximately 4.6, a slightly stronger acid than acetic acid (30).

2.3 OTHER ORGANOMETALLIC COMPLEXES CONTAINING TRANSITION METALS

A third class of compounds to be studied in this report is slightly different from those described in Sections 2.1 and 2.2. The type of organometallic complexes of interest are: (i) reactive organometallic complexes such as Ni(1,5-cyclooctadiene)$_2$,(Ni(1,5-COD)$_2$) (31) whose ligands, the 1,5-cyclooctadiene in this case can be easily displaced by another ligand; and (ii) compounds such as (olefin)(diketonato)-metal complexes (32, 33), whose interest arise from similar studies involving bis(diketonato)metal complexes studied in Section 2.2.

The first type of organometallic complex described above is very common, and is employed extensively as homogeneous catalysts for various reactions. A more detailed discussion on the second type of complex will be carried out here. Doyle et al (32) studied compounds of the type [Cu(diketonato)]$_n$L$_m$ (L = CO, alkene or diene; n and m = 1 or 2). It was found that complexes with L=CO or light olefins were unstable; however, the non volatile alkenes and dienes formed isolable complexes. The preparation is usually carried out as follows:

copper(I) oxide + diketone → copper(I)(diketonate) [1]

copper(I)(diketonate) + CO → copper(carbonyl)(ß-diketonato) [2]

Examples of diketones that are employed to synthesize these derivatives are: hexafluoroacetylacetonate, trifluoro-acetylacetonate, thenoyltrifluoroacetonate, and (trifluoroacetyl)-camphor. The presence of carbon monoxide and olefins is necessary for reaction [2] to proceed (32). In its absence, the equilibrium

will lie on the side of the copper(I)(diketonate) which is unstable and will disproportionate to copper metal and copper(II)(diketonate). Similarly, if the diketonate anion is not capable of stabilizing the carbonyl adduct, as is the case with acetylacetonate and alkyl- and aryl-substituted acetylacetonates, the same disproportionation reaction will occur. Since the disproportionation is an equilibrium reaction, a carbonyl copper(I)(diketonate) derivative can be formed from copper metal and certain copper(II)(diketonate) (32). This has been found to be successful with bis(hexafluoroacetylacetonate)copper(II). In this type of complex, the CO adduct is easily displaced by other ligands, for example, phosphines, amines, isonitriles.

The metal-(diketonato) complexes derived with C_2 to C_4 olefins are nearly identical with the CO complex with regard to their methods of preparation, composition, chemical reactivity, and stability. Higher olefins react in a manner similar to the lower homologues but, presumably due to their lower volatility, the copper(I)(diketonate) complexes formed from them can often be isolated in a relatively pure form. For most simple olefins including styrene, 1-decene, cyclooctene, norbornene, and the like, the hexafluoroacetylacetonato complexes are isolated as yellow or greenish yellow oils or solids containing 1 mole of olefin per copper atom. Depending on the particular olefin and the diketone groups, the complexes are more or less unstable with respect to air oxidation and disproportionation but are moisture insensitive. In general those complexes derived from hexafluoroacetylacetone are more stable than those prepared from trifluoroacetylacetone, thenoyltrifluoroacetone, and (trifluoroacetyl)camphor. In a few cases the complexes isolated appear to have 2 moles of olefin per copper. The factors determining the number of olefin ligands coordinated to the copper are not fully understood. However, with the possible release of carbon monoxide, this type of compound may not be a good candidate to be used as activated carbon impregnant.

The reaction of dienes with Cu_2O and a sterically unhindered fluorinated diketone yields complexes with either one or two atoms of copper per diene depending on the particular diene chosen. Both 1,5-cyclooctadiene (1,5-COD) and 1,3-butadiene give complexes with the composition Cu(diketonato)·(diene) whereas norbornadiene and isoprene appear to give complexes which were analyzed as (diene)·[Cu(diketonato)]$_2$. The cyclooctadiene and norbornadiene complexes are stable yellow solids which can be handled in air for short periods of time without decomposition (32).

The structures of the [(1,5-COD)CuCl]$_2$ and Cu·(hfac)·(1,5-COD) complexes determined from ^{1}H NMR indicated that the latter may have a chelated structure, or a fluxional process with the copper alternately bound to one of two double bonds of the cyclooctadiene (32). It is useful to note that aromatic hydrocarbons such as benzene and toluene are suitable solvents for the synthesis of

Cu(I)(diketonates) since they do not interact with these complexes (32).

Similar experimental procedures can be used to synthesize silver analogues of the compounds discussed above. These silver complexes are white crystalline solids. They closely parallel each other in terms of stability and composition. One difference between the copper and silver complexes is that the Ag(I)(diketonate) are not subject to disproportionation and loss of the ligands and do not lead to deposition of silver (32). Partenheimer and Johnson (33) prepared several silver olefin compounds of the type Ag(diketonato)·(olefin), and have established that the silver(I) cation has a strong propensity to react with olefins to form labile, relatively weakly bonded olefin complexes. The complexes synthesized are easily isolable and soluble in relatively nonpolar solvents such as dichloromethane or cyclohexane. The preparation of these complexes differed from that described for the copper analogues, and can be summarized by the following reactions:

$$AgNO_3 + \text{olefin} \rightarrow [Ag(\text{olefin})]^+NO_3^- \quad [3]$$

$$[Ag(\text{olefin})]^+NO_3^- + Na^+hfac^- \rightarrow [Ag(\text{olefin})\cdot(hfac)] + NaNO_3 \quad [4]$$

Reactions [3] and [4] also occurred when trifluoroacetylacetonate was used. The type of diketone used in the synthesis affects the stability of the product. For example, Ag(hfac)·(1,5-COD) is much more stable than the trifluoroacetylacetonate analogue. Partenheimer attempted the synthesis of analogous compounds using the conjugate base of acetylacetone, but failed. One conjecture is that stability of these compounds is inversely proportional to the basicity of the acetylacetonate derivative used (33). Furthermore, it has been shown by ^1H NMR that the olefin dissociates rapidly from the Ag(tfac) or Ag(hfac) moieties in solution. The type of solvent used apparently has an effect on the arrangement of the complexes. For instance, Ag(hfac)·(1,5-COD) and Ag(hfac)·(cyclooctene) exist as monomers in bromoform, while Ag(hfac)·(1,5-COD) is partially polymerized in cyclohexane (33).

3.0 MATERIALS AND EQUIPMENT

3.1 STARTING MATERIALS PROCURED FROM COMMERCIAL SOURCES

Table 1 lists all the chemicals used in this study which were obtained from commercial sources.

TABLE 1: Chemicals Employed

Chemical	Formula/Molecular Mass	Melting/Boiling Point (°C)	Appearance & Spectroscopic Identification	Supplier[1]
Chromium nitrate nanohydrate	$Cr(NO_3)_3 \cdot 9H_2O$ 400.15	m.p. 60°C	black crystals	1
Chromium(III) acetylacetonate	$[CH_3COCH=C(O-)CH_3]_3Cr$ 349.33	m.p. 210°C	purple powder FTIR (Figure 1)	1
Cobalt(III) acetylacetonate	$[CH_3COCH=C(O-)CH_3]_3Co$ 356.26	m/p. 211°C (dec.)	green crystals FTIR (Figure 2)	1
Cobalt(II) acetylacetonate hydrate	$[CH_3COCH=C(O-)CH_3]_2Co \cdot H_2O$ 757.15	m.p. 165-170°C	reddish brown powder FTIR (Figure 3)	1
Cobalt(II) hexaflucroacetyl-acetonate hydrate	$[CF_3COCH=C(O-)CF_3]_2Co \cdot H_2O$ 473.04	m.p. 197°C (dec)	orange powder FTIR (Figure 4)	1
Copper(II) acetate monohydrate	$(CH_3CO_2)_2Cu \cdot H_2O$ 199.65	m.p. 115°C	blue green powder	1
Copper(II) chloride	$CuCl_2$	m.p. 620°C	brown powder FTIR (Figure 5)	1
Copper(II) hexafluoroacetyl-acetonate hydrate	$[CF_3COCH=C(O-)CF_3]_2Cu \cdot H_2O$ 495.66	m.p. 130-134°C	green crystals FTIR (Figure 6) UV/VIS (Figures 7,8)	1
Copper(I) oxide	Cu_2O / 143.08	m.p. 1235°C	red powder	1
1,3-Cyclo-hexadiene	C_6H_8 80.13	b.p. 80°C	colorless liquid	1
1,4-Cyclo-hexadiene	C_6H_8 80.13	b.p. 81-82°C	colorless liquid	1
1,5-Cyclo-octadiene	C_8H_{12} 108.18	b.p. 149-150°C	colorless liquid	1
2,4-Pentanedione	$CH_3COCH_2COCH_3$ 100.12	b.p. 140°C	colorless liquid	1

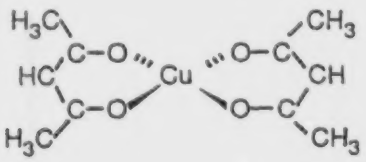
TABLE 1: Chemicals Employed (Cont'd)

Chemical	Formula/Molecular Mass	Melting/Boiling Point (°C)	Appearance & Spectroscopic Identification	Supplier[1]
1,1,1,5,5,5-hexafluoropentane -2,4-dione	$CF_3COCH_2COCF_3$ 208.06	b.p. 70-71°C	colorless liquid	1
Triethylenediamine (TEDA)	$C_6H_{12}N_2$ 112.18	m.p. 158-160°C (subl.)	white crystals FTIR (Figure 9)	1
Quinuclidine (QUIN)	$C_7H_{13}N$ 111.19	m.p. 157-160°C (subl.)	white crystals FTIR (Figure 10)	2
Silver Nitrate	$AgNO_3$ 169.88	m.p. 212°C	white crystals	3
Sodium Hydroxide	NaOH 40.00	m.p. 318.4°C	white pellets	4

[1] Suppliers:
1 - Aldrich Chemical Co., Milwaukee, Wisconsin, USA
2 - Fluka Chemical Corp., Ronkonkoma, New York, USA
3 - Engelhard Industries of Canada, Montreal, Canada
4 - Mallinckrodt Inc., Paris, Kentucky, USA

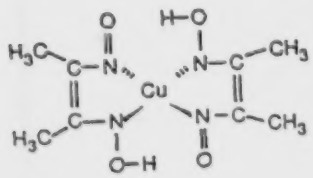
3.2 CHEMICALS SYNTHESIZED AT DREO

a. Copper(II) acetylacetonate



Formula = $[CH_3COCH{=}C(O{-})CH_3]_2Cu$
MW = 263.78
Synonyms: Bis(acetylacetono) copper(II), Copper(2,4-pentanedione)
Melting Point: 245-250°C (dec)
Boiling Point: sublimes
Appearance: fine blue powder
FTIR spectrum is shown in Figure 11

b. Copper(II) dimethylglyoxime



Formula = $[CH_3C(=NOH)C(-NOH)CH_3]_2Cu$
MW = 281.67
Melting Point: >250°C (unrecrystallized)
Appearance: brown powder
FTIR spectrum is shown in Figure 12
UV/VIS spectrum is shown in Figure 13

c. Copper(II) laurate
Formula = $[O_2C(CH_2)_{10}CH_3]_2Cu$
MW = 462.17
Melting Point: 109°C (111-113°C, CRC handbook)
Appearance: pale blue solid
FTIR spectrum is shown in Figure 14

3.3 FOURIER TRANSFORM INFRARED (FTIR) MEASUREMENTS

All FTIR spectra were recorded between 4000 and 450 cm^{-1} on a Perkin Elmer 1750 Fourier transform infrared spectrometer using nujol mulls on KBr or ZnSe discs. Typically 5-10 scans gave an effective resolution.

3.4 NUCLEAR MAGNETIC RESONANCE (NMR) MEASUREMENTS

Typical ^1H NMR spectra were recorded on a Varian XL-200 NMR spectrometer at 200 MHz. Chemical shifts for all spectra were referenced to TMS (tetramethylsilane).

3.5 ULTRAVIOLET/VISIBLE (UV/VIS) MEASUREMENTS

All UV/VIS spectra were recorded on a Hewlett-Packard 89500 UV/VIS ChemStation and 8452 Diode Array spectrophotometer. The solution to be investigated was put into 1 cm light path high quality quartz (190-820 nm) cell. A solvent blank was run before and after each scan.

4.0 SYNTHETIC PROCEDURES FOR THE TRANSITION METAL COMPLEXES

There were three types of organometallic complexes prepared in this study. The first type consisted of transition-metal complexes containing triethylenediamine (TEDA) or quinuclidine (QUIN). The reactions were carried out by the addition of TEDA (or QUIN) to a solution containing the salt of the transition metals. The transition metals investigated were copper, chromium and silver. The second type consisted of the bis(hfac)metal·(TEDA) or bis(hfac)metal·(QUIN) (where metal = copper, or cobalt) type complexes. The third type of complexes contained olefins (such as 1,5-cyclooctadiene and 1,4-cyclohexadiene, etc.) and bis(hfac)metal. The transition metals studied included copper, cobalt and silver. Some of these syntheses had been reported in the literature, and therefore will not be reproduced here.

In the next three sections, the preparation of some of the precursors used in the synthesis (Section 4.1), some typical preparation procedures (Section 4.2), and the general schemes of preparations and characterizations (Section 4.3) will be presented.

4.1 PREPARATION OF SOME PRECURSOR COMPOUNDS

Most of the chemicals used in this study were purchased from various chemical suppliers (Sections 3.1 to 3.4). For the compounds which were custom synthesized here at DREO, their

preparative procedures are given below. Compounds were identified by their physical and spectroscopic properties.

4.1.1 $Cu(laurate)_2$

Copper acetate hydrate (1.72 g, 8.61 mmole) were dissolved in 100 mL of ethanol. To this clear bluish-green solution was added 3.49 g of lauric acid (17.45 mmole) dissolved in 25 mL ethanol. No immediate reaction was observed. After about ½ hour, a blue precipitate appeared. More precipitate appeared after stirring for 18 hours. The melting point of copper laurate is 109°C, and the yield of the crude product is about 90%.

4.1.2 $Cu(acac)_2$

Copper acetate monohydrate (9.61 g, 48 mmole) was dissolved in 150 mL of deionized distilled water. To this bluish solution was then added 9.86 mL of 2,4-pentanedione (acetylacetone) (96 mmole) via a syringe. The blue solution turned cloudy immediately. A fine precipitate was formed. 25 mL of 4M NaOH solution was then added to this solution and the reaction mixture was heated at about 60°C for 10 minutes. After filtration, a blue solid was obtained. Yield was 86%.

4.1.3 $Cu(dmg)_2$

Copper acetate monohydrate (6.3 g, 31.6 mmole) was dissolved in 100 mL of ethanol, which resulted in a green solution. A solution containing 7.3 g (62.9 mmole) of dimethylglyoxime (dmg) dissolved in 300 mL of ethanol was added to the copper solution which turned black immediately and became opaque. On filtration, a brown precipitate, $Cu(dmg)_2$, was obtained. All attempts at recrystallization failed (no suitable solvent was found). The yield was 23%.

4.2 TYPICAL SYNTHETIC PROCEDURES

All the transition metal complexes studied in this report were synthesized by three main routes. The first one was a simple addition of all ingredients into one reaction vessel, e.g. the reaction between the metal salts and triethylenediamine. The second synthetic route was employed in the preparation of the Cu(hfac)·(1,5-COD) type complexes, which were done in a dry, oxygen-free atmosphere. The last synthetic procedure was characterized by the preparation of the Ag(hfac)·(1,5-COD) type complex, which involved a very elaborate procedure. All three procedures are discussed below.

4.2.1 Preparative Procedure "A"

A typical example of preparative procedure "A" is given below in the preparation of $Cu(hfac)_2 \cdot TEDA$. A 1:1 molar mixture of $Cu(hfac)_2 \cdot H_2O$ (4.99 g, 10.07 mmole) and TEDA (1.19 g, 10.63 mmole) in CCl_4 was made by adding solid TEDA to the blue-green solution of $Cu(hfac)_2 \cdot H_2O$ in CCl_4. Immediately following the addition of TEDA a reddish-brown solid formed on the walls of the reaction flask. The solution was refluxed at 45-50°C, with stirring, using an oil bath, for 30 minutes. The now yellow-green solution was then removed from the oil bath and allowed to return to room temperature. This was then placed in an ice bath for 15 minutes. The contents of the reaction flask were then suction filtered through a Buchner funnel, leaving a yellow-green, flaky solid, and a dark green filtrate. The crude product, left to dry in air, was produced at a 90% yield.

4.2.2 Preparative Procedure "B"

A typical example of preparative procedure "B" is given by the synthesis of $Cu(hfac) \cdot (1,5\text{-COD})$. Cuprous oxide, Cu_2O (1,43 g, 9.99 mmole) was stirred with 2.5 mL (2.2 g, 20.4 mmole) of 1,5-cyclooctadiene (1,5-COD) in 75 mL of dry tetrahydrofuran (THF). The THF was distilled directly into the pre-dried 250 mL 3-neck round-bottom flask under a stream of nitrogen. This gave a red suspension. 1,1,1,5,5,5-hexafluoro-pentane-2,4-dione (hfac) (4.28 g, 20.6 mmole) was added to 50 mL of dry THF and this solution was then added drop-wise to the 1,5-COD solution through a dropping funnel over a period of 40 minutes. Afterwards, the red suspension took on a yellow tinge. After 3 hours of stirring under a blanket of nitrogen, a yellow solution with a red precipitate was observed. Suction filtration in air yielded a clear yellow filtrate. All the THF was removed by rotary evaporation at 40°C which left a yellow crystalline residue with a green tint. The yield was >100% indicating the presence of impurities. This compound is air/moisture sensitive, and decomposes after several days to a green compound.

4.2.3 Preparative Procedure "C"

A typical example of preparative procedure "C" is given by the synthetic route of $Ag(hfac) \cdot (1,5\text{-COD})$. A solution of $Na^+(hfac)^-$ was prepared by adding 1,1,1,5,5,5-hexafluoropentane-2,4-dione (5.88 g, 28.1 mmole) to a few mL of distilled water, followed by the addition of sodium hydroxide pellets (1.125 g, 28.1 mmole) with stirring. In another beaker, silver nitrate (5.92 g, 34.9 mmole) was dissolved in 30 mL of distilled water. 4 mL of 1,5-cyclooctadiene (3.53 g, 32.5 mmole) was then syringed into the silver nitrate solution. The Na(hfac) solution prepared earlier was then added to this solution containing silver nitrate/1,5-COD mixture. The reaction mixture turned a light brown colour with the

appearance of some thick, light brown precipitate. On filtration, a brown residue was obtained. Yield was 66% based on a formula of Ag(hfac)·(1,5-COD), with the hfac being the limiting reagent.

4.3 GENERAL SCHEMES OF PREPARATION AND CHARACTERIZATIONS

Tables 2, 3 and 4 summarize the preparative method, the reference to the preparative route (if any), the amount of reagent and solvent, and the temperature employed in the synthesis of the organometallic complexes. Furthermore, these tables also include the colour of the complex prepared, the yield, the melting point, solubility, and the spectroscopic techniques used to identify these complexes.

5.0 DISCUSSION

5.1 PREPARATION AND PHYSICAL DATA OF METAL SALTS AND TEDA/QUIN COMPLEXES

The preparation of these complexes was straightforward. The 1:1 or 1:2 addition of the metal salts to TEDA/QUIN in a suitable solvent was carried out accordingly. In this section, any peculiarities in the preparative step, or in the physical and spectroscopic characteristics will be discussed. For the complete characterization of organometallic complexes, ultrapure samples of the complexes and expensive analyical instruments such as X-ray crystallography and elemental analysis, etc. are required. However, since all these organometallic complexes are going to be screened as chemical impregnants for activated carbon only, having very high purity samples of these complexes is not essential. Thus for the present purpose, all spectra data and melting point determinations were made on the synthesized complexes directly, and on the recrystallized products only if suitable solvent was found.

Some of the complexes reported here have been synthesized before, thus the same chemical formula was used for the synthesized complex prepared here, e.g. $Cu(laurate)_2 \cdot 1/2(TEDA)$. For similar complexes using the same synthetic procedure, the same formula may not necessarily apply, e.g. the reaction between $Cu(laurate)_2$ and quinuclidine. Thus the formula $Cu(laurate)_2 \cdot x(QUIN)$ was used to signify that the chemical formula was not ascertained. It was anticipated that if a certain organometallic complex performed effectively as a chemical impregnant, this complex would then be characterized carefully to ascertain the true formula and composition. Thus in this section, only the physical and spectral data were recorded, without any characterization at all on the synthesized complexes. In cases where physical and spectral data were available, comparisons were made with experimental data.

P143922.PDF [Page: 29 of 81]

TABLE 2: Metal Salts and TEDA/QUIN Complexes

Complex	Ref	Prep Method[1]	Amount of Reagent Used (mmole)	Solvent/ Volume (mL)	Temp of Reaction (°C)	Colour Compound	Yield[2] (%)	Melting Point[3] (°C)	Spectral Data[4]	Solvents
$CuCl_2$·(TEDA)	10	A	$CuCl_2$, 9.7 TEDA, 10.1	Ethanol/70	25	orange brown ppt	70	>180	FTIR (15)	None
$CuCl_2$·(QUIN)	10	A	$CuCl_2$, 10.0 QUIN, 10.2	Ethanol/70	25	orange ppt	73	>180	FTIR (16)	None
$Cu(laurate)_2$·½(TEDA)	7	A	$Cu(laurate)_2$, 1.0 TEDA, 1.1	Dimethyl-formamide/100	25	green ppt	82	110-115	FTIR (17)	None
$Cu(laurate)_2$·x(QUIN)	-	A	$Cu(laurate)_2$, 24.9 QUIN, 25.1	Dimethyl-formamide/500	25	green ppt	91	45-47	FTIR (18)	$CHCl_3$, CCl_4
$Cu(acetate)_2$·½(TEDA)	7	A	$Cu(acetate)_2$, 25.1 TEDA, 13	Dimethyl-formamide/300	25	green ppt	92	>230	FTIR (19) UV/VIS (20)	None
$Cr(NO_3)_3$·x(TEDA)	-	A	$Cr(NO_3)_3$·$9H_2O$, 12.6 TEDA, 25.3	Ethanol/110	25	bluish green ppt	100	170-171	FTIR (21)	None
$Cr(NO_3)_3$·x(QUIN)	-	A	$Cr(NO_3)_3$·$9H_2O$, 24.9 QUIN, 49.9	Ethanol/100	25	greyish blue ppt	Poor	>170	FTIR (22)	None
$AgNO_3$·x(TEDA) $1<x<2$	6	A	$AgNO_3$, 9.7 TEDA, 10.0	Acetonitrile/90	25	white ppt	>100%[5]	>170	FTIR (23)	None
$AgNO_3$·2(QUIN)	6	A	$AgNO_3$, 9.7 QUIN, 20	Acetonitrile/100	No Reaction[6]					

Notes: 1 Preparation methods as reported in Section 4.2.

2 This is the yield of crude product.

3 For compounds which decompose, or change color upon heating, their melting points are given in (> X °C, where X = temperature at which decomposition or change occurs.

4 In spectral data, FTIR = Fourier Transform Infrared Spectrum, UV/VIS = Ultra Violet/Visible Spectrum, ^{1}H NMR = Proton Nuclear Magnetic Resonance Spectrum. The number inside the bracket after the spectroscopic technique indicates the Figure number in which the spectrum would be found.

5 From the yield, the stoichiometry of this complex is neither $AgNO_3$·(TEDA), nor $AgNO_3$·1.5(TEDA) as suggested in Ref (18). Thus a stoichiometry of $AgNO_3$·x(TEDA), where $1<x<2$, was suggested.

6 There was no observed reaction even if the reaction was carried out at high temperatures (~60°C) or in total darkness, contrasting to previous claims by Ref (18).

P143922.PDF [Page: 30 of 81]

TABLE 3: Metal Acetylacetonates and TEDA/QUIN Complexes

Complex	Ref	Prep Method[1]	Amount of Reagent Used (mmole)	Solvent/ Volume (mL)	Temp. of Reaction (°C)	Color of Compound	Yield[2] (%)	Melting Point[3] (°C)	Spectral Data[4]	Solvents
$Cu(hfac)_2 \cdot$ (TEDA)	15	A	$Cu(hfac)_2 \cdot H_2O$, 10.07 TEDA, 10.63	CCl_4/100	50	reddish brown ppt	90	130-132	FTIR (24) UV/VIS (25,26)	All solvent except H_2O, hexane, isopropanol, CCl_4
$Cu(hfac)_2 \cdot$ (QUIN)	-	A	$Cu(hfac)_2 \cdot H_2O$, 9.91 QUIN, 9.79	CCl_4/50	75	No Reaction				
$Cu(acac)_2$ (TEDA)	-	A	$Cu(acac)_2$, 6.1 TEDA, 6.3	Ethanol/100	55	No Reaction				
$Cu(acac)_2 \cdot x$(QUIN)	-	A	$Cu(acac)_2$, 10.00 QUIN, 9.91	CCl_4/20	70	reddish brown ppt	99	195-205	FTIR (27)	CH_2Cl_2
$Co(acac)_2 \cdot x$(TEDA) $1<x<2$		A	$Co(acac)_2 \cdot H_2O$, 10.3 TEDA, 20.9	THF/75	25	greenish brown ppt	65	>250	FTIR (28)	Not determined
$Co(acac)_2 \cdot x$(QUIN)	-	A	$Co(acac)_2 \cdot H_2O$, 10.0 QUIN, 10.0	THF/35	70	greenish brown ppt	poor	>180	FTIR (29)	Not determined
$Co(hfac)_2 \cdot x$(TEDA)	-	A	$Co(hfac)_2 \cdot H_2O$, 9.5 TEDA, 18.5	Acetone/50	25	orange brown ppt	79	>250	FTIR (30)	Not determined
$Co(hfac)_2$ (QUIN)	-	A	$Co(hfac)_2 \cdot H_2O$, 8.56 QUIN, 10.0	DMF/500	55	No Reaction				
$Co(acac)_3 \cdot$ (TEDA)	-	A	$Co(acac)_3$, 11.9 TEDA, 24.8	CH_2Cl_2/90	60	No Reaction				
$Co(acac)_3$ (QUIN)	-	A	$Co(acac)_3$, 11.0 QUIN, 11.0	CCl_4/120	55	No Reaction				

P143922.PDF [Page: 31 of 81]

TABLE 3: Metal Acetylacetonates and TEDA/QUIN Complexes (Cont'd)

Complex	Ref	Prep Method[1]	Amount of Reagent Used (mmole)	Solvent/ Volume (mL)	Temp of Reaction (°C)	Color of Compound	Yield[2] (%)	Melting Point[3] (°C)	Spectral Data[4]	Solvents
$Cr(acac)_3$2(TEDA)	-	A	$Cr(acac)_3$, 12.4 TEDA, 21.7	CH_2Cl_2/100	60	No Reaction				
$Cr(acac)_3$2(QUIN)	-	A	$Cr(acac)_3$, 12.4 QUIN, 20.1	CH_2Cl_2/100	60	No Reaction				

Notes 1. Preparation methods as reported in Section 4.2.

2 This is the yield of crude product.

3 For compounds which decompose, or change color upon heating, their melting points are given in (> X °C, where X = temperature at which decomposition or change occurs.

4 In spectral data, FTIR = Fourier Transform Infrared Spectrum, UV/VIS = Ultra Violet/Visible Spectrum, ^{1}H NMR = Proton Nuclear Magnetic Resonance Spectrum. The number inside the bracket after the spectroscopic technique indicates the Figure number in which the spectrum would be found.

P143922.PDF [Page: 32 of 81]

TABLE 4: Other Complexes

Complex	Ref	Prep Method[1]	Amount of Reagent Used (mmole)	Solvent/ Volume (mL)	Temp of Reaction (°C)	Color of Compound	Yield[2] (%)	Melting Point[3] (°C)	Spectral Data[4]	Solvents
Cu(hfac)·(1,5-COD)	23	B	Cu_2O, 9.99 1,5-COD, 20.4 hfac, 20.6	THF/125	25	yellow crystal	>100 (based on copper)	74	FTIR (31) ^{1}H NMR (32)	$CHCl_3$
Cu(hfac)$_2$·(1,3-CHD)	-	B	Cu_2O, 10.3 1,3-CHD, 20.8 hfac, 19.8	THF/125	25	green ppt	>100 (based on copper)	>230	Not done, product unstable	CH_2Cl_2
Cu(dmg)$_2$ (TEDA)	-	A	Cu(dmg)$_2$, 1.77 TEDA, 1.77	Ethylene chloride/50	25	brown ppt	75	>230	FTIR (33) UV/VIS (34)	slightly in CH_2Cl_2
Co(hfac)·(1,5-COD)	-	A	Co(hfac)·H_2O, 8.6 1,5-COD, 8.6	THF/250	25	No Reaction				
Co(acac)$_2$·(1,5-COD)	-	A	Co(acac)$_2$, 4.7 1,5-COD, 24.5	Methanol/200	25	No Reaction				
Co(acac)$_3$·(1,5-COD)	-	A	Co(acac)$_3$, 11.0 1,5-COD, 11.0	THF/100 CH_2Cl_2/20	25	No Reaction				
Ag(hfac)·(1,5-COD)	33	C	NaOH, 28.1 hfac, 28.1 $AgNO_3$, 34.9 1,5-COD, 32.5	H_2O/40	25	brown ppt	66	120-122	FTIR (35) ^{1}H NMR (36)	$CHCl_3$
Ag(hfac)·(1,4-CHD)	-	C	NaOH, 28.1 hfac, 28.1 $AgNO_3$, 34.9 1,4-CHD, 35.4	H_2O/40	25	brown ppt	49	120-122	FTIR (37) ^{1}H NMR (38)	$CHCl_3$

Notes 1 Preparation methods as reported in Section 4.2

2 This is the yield of crude produce

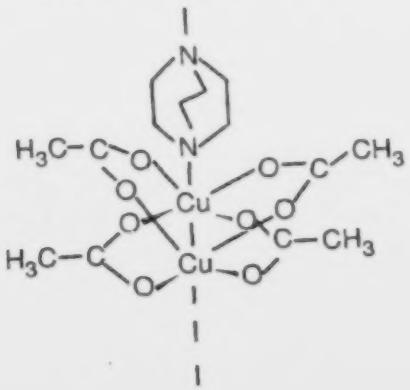
3 For compounds which decompose, or change color upon heating, their melting points are given in (> X °C, where X = temperataure at which decomposition or change occurs

4 In spectral data, FTIR = Fourier Transform Infrared Spectrum, UV/VIS = Ultra Violet/Visible Spectrum, ^{1}H NMR = Proton Nuclear Magnetic Resonance Spectrum The number inside the bracket after the spectroscopic technique indicates the Figure number in which the spectrum would be found

5.1.1 Copper Complexes

Most of the copper complexes synthesized in this section have been previously reported (7,10). There were no observed anomalies in the synthesis of these complexes. However, the melting point for $CuCl_2 \cdot$(TEDA) measured in this laboratory was greater than 180°C, at which point the complex was observed to decompose. This could be due to the presence of impurities. There were inconsistencies in previous reports concerning this melting point, it has been reported 187-192°C in Ref (10) or 230°C in Ref (34). Similarly, for $CuCl_2 \cdot$(QUIN), the melting point measured in this laboratory was >180°C, but a temperature range of 164-166°C was reported in Ref. (10). One interesting complex obtained in this laboratory (never prepared before), Cu(laurate)$_2 \cdot$(QUIN), has a melting point of 45-47°C only, in contrast with other copper salts and TEDA/QUIN complexes. Its analog, Cu(laurate)$_2 \cdot \frac{1}{2}$(TEDA) also has a low melting point of 110-115°C, which is lower than the 170-230°C range observed for other complexes. It is well known that organometallic complexes involving transition metals have high melting points (3), and the reason for this irregularity is not obvious.

$Cu(O_2CCH_3)_2 \cdot 1/2(TEDA)$



FTIR spectra were recorded for the copper complexes synthesized in this Section. All observed spectra contain absorption bands characteristic of the copper salt and the TEDA/QUIN molecule, i.e. they are composite spectra consisting of both the copper salt and the TEDA/QUIN molecule. However, there is a small shift of the bands between 750 and 1100 cm^{-1} (which are characteristic bands contributed from TEDA or QUIN molecule) to higher frequency. This is obvious because the high symmetry which exists within the TEDA molecule (lower symmetry in QUIN) is now distorted because of the bonding of nitrogen atom (on the TEDA/QUIN molecule) towards the central copper atom.

The FTIR spectra of $CuCl_2 \cdot$(TEDA) and $CuCl_2 \cdot$(QUIN) are quite similar, which is to be expected. The same observation applies to FTIR spectra for Cu(laurate)$_2 \cdot \frac{1}{2}$(TEDA) and Cu(laurate)$_2 \cdot$(QUIN) and Cu(acetate)$_2 \cdot \frac{1}{2}$(TEDA). Furthermore, the FTIR spectrum obtained for Cu(laurate)$_2 \cdot \frac{1}{2}$(TEDA) is very similar to the one previously obtained (7).

In general, no suitable solvent was found for all copper complexes synthesized, except Cu(laurate)$_2 \cdot \frac{1}{2}$(TEDA) and Cu(laurate)$_2 \cdot$(QUIN) which are soluble in chlorinated hydrocarbons.

5.1.2 Chromium Complexes

Only two complexes were prepared in this category, i.e. $Cr(NO_3)_3 \cdot x$(TEDA) and $Cr(NO_3)_3 \cdot x$(QUIN), both of them have not been reported before. For the preparation involving $Cr(NO_3)_3$ and TEDA and QUIN, both 1:1 and 1:2 molar ratio were employed. The same product, identified from melting points and FTIR spectra was obtained, thus the stoichiometry of $Cr(NO_3)_3 \cdot 2$(TEDA) and $Cr(NO_3)_3 \cdot 2$(QUIN) may be used for the reaction products.

Similar to the copper complexes, the FTIR spectra of these chromium complexes are very close to the composite spectra of $Cr(NO_3)_3$ and TEDA/QUIN. No suitable solvent was obtained for these chromium complexes.

5.1.3 Silver Complexes

The two silver complexes synthesized in this Section have both been reported previously (8). However, in the synthesis of the complex between $AgNO_3$ and TEDA, the same product (identified by the same melting point and FTIR spectra) was obtained when the molar ratio of $AgNO_3$ to TEDA was increased from 1:1 to 2:3. This is inconsistent to that reported in Ref (8). After the crude product was recrystallized (from a 10:1 (by volume) of acetone: NH_4OH solution) and dried, the yield was found to be greater than 100%. This probably indicated that the correct stoichiometry may be $AgNO_3 \cdot 2$(TEDA). However, the complex was assigned a formula of $AgNO_3 \cdot x$(TEDA) ($1<x<2$) until the structure can be ascertained by x-ray crystallography. It has been reported (8) that a melting point of 154-155°C was obtained for $AgNO_3 \cdot 1.5$ TEDA, but this was not observed in our characterization. The FTIR spectrum of $AgNO_3 \cdot x$(TEDA) shows absorption bands characteristic of both $AgNO_3$ and TEDA.

The synthesis of $AgNO_3 \cdot 2$(QUIN) was unsuccessful. Only a greyish precipitate (identified as Ag_2O from FTIR) was obtained from the reaction mixture. FTIR analysis of the solution showed a composite of absorption bands arising from quinuclidine and acetonitrile only. In the literature (8), it was claimed that this

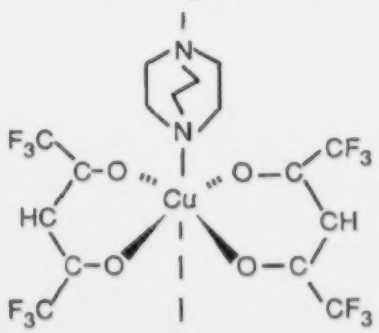
complex, $AgNO_3 \cdot 2(QUIN)$ is a white powder precipitated from the reaction mixture. Numerous unsuccessful attempts of this synthesis (some were carried out in total darkness - to inhibit the formation of Ag_2O) were carried out. No reason for the failure of this literature procedure was readily apparent.

5.2 PREPARATION AND PHYSICAL DATA METAL ACETYLACETONATES AND TEDA/QUIN COMPLEXES

5.2.1 Copper Complexes

According to the literature (15), $Cu(acac)_2$ does not form a complex with TEDA, but $Cu(hfac)_2$ does. This is indeed the case and was observed by this laboratory. However, when the similar synthesis of $Cu(hfac)_2 \cdot (QUIN)$, and $Cu(acac)_2 \cdot (QUIN)$ were attempted, only the preparation of $Cu(acac)_2 \cdot (QUIN)$ was successful. It seems that the coordination chemistry of these complexes (and their formation) depends on both the electrostatic effect of the $-CF_3$ substituent (vs - CH_3 group), and the alkalinity of quinuclidine vs triethylenediamine.

$Cu(hfac)_2.TEDA$



The characterization of these two complexes, $Cu(hfac)_2 \cdot (TEDA)$ and $Cu(acac)_2 \cdot (QUIN)$ was straightforward. The FTIR spectrum of $Cu(hfac)_2 \cdot (TEDA)$ (Figure 24) shows absorption bands characteristic to both $Cu(hfac)_2 \cdot xH_2O$ and TEDA. Absorption bands observed at 1640, 1558, 1532 and 1253 cm^{-1} (for C=O and C=C bands) coincide with those previously reported (15). UV/VIS spectra of this yellowish-green complex from 320 to 520 nm and from 600 to 800 nm respectively are shown in Figures 25 and 26. The λ_{max} for $Cu(hfac)_2 \cdot xH_2O$ occurs at 310 and 685 nm, which is quite different from those of $Cu(hfac)_2 \cdot (TEDA)$ observed at 322, 404 and 609 nm respectively. The complex $Cu(hfac)_2 \cdot (TEDA)$ is soluble in various solvents, but not very soluble in water, hexane, isopropanol and carbon tetrachloride.

The characterization of $Cu(acac)_2 \cdot (QUIN)$ was similar to that of $Cu(hfac)_2 \cdot (TEDA)$.

5.2.2 Cobalt Complexes

The detailed synthetic procedure for $Co(acac)_2 \cdot x(TEDA)$ $(1<x<2)$ is unknown, although the reaction has been described as spontaneous (23). During the preparation of this complex, the same complex (identified by melting point and FTIR) was obtained when the ratio of $Co(acac)_2 \cdot H_2O$ to TEDA was raised from 1:1 to 1:2. Thus the formula of this complex was designated as $Co(acac)_2 \cdot x(TEDA)$ $(1<x<2)$ until more spectral data is obtained. While it has never been reported, the 1:1 molar addition of cobalt acetylacetonates and its fluoro-derivative to TEDA/QUIN produced several complexes, namely, $Co(acac)_2 \cdot x(TEDA)$, $Co(acac)_2 \cdot (QUIN)$ and $Co(hfac)_2 \cdot (QUIN)$. All reaction between $Co(acac)_3$ and TEDA/QUIN was unsuccessful probably because the coordination sphere around the central cobalt atom was full (with three acetylacetonato ligands surrounding the central metal atom) and TEDA/QUIN was not a strong enough nucleophile to displace one of these acetylacetone molecule.

It is interesting to note that both $Co(acac)_2$ and $Co(hfac)_2$ reacted with TEDA to yield the corresponding $Co(acac)_2 \cdot (TEDA)$ and $Co(hfac)_2 \cdot (TEDA)$ complexes. This is in contrast to the discussion in Section 5.2.1, in which only $Cu(hfac)_2 \cdot (TEDA)$ complex was formed, but not $Cu(acac)_2 \cdot (TEDA)$. The reaction between QUIN and $Co(acac)_2$ gave very poor yield, and there was no reaction between $Co(hfac)_2$ and QUIN. This result is consistent with the observations made with the reactions between $Cu(acac)_2$ and $Cu(hfac)_2$ with QUIN.

The characterization of these cobalt complexes were done exclusively with FTIR spectroscopy. These spectra are very similar to those obtained for $Cu(hfac)_2 \cdot (TEDA)$ or $Cu(acac)_2 \cdot (QUIN)$. For example, in Figure 28, the characteristic -OH band observed for $Co(acac)_2 \cdot xH_2O$ (shown earlier in Figure 2) has disappeared, and the absorption bands in this figure are typical of TEDA and $Co(acac)_2$.

5.2.3 Chromium Complexes

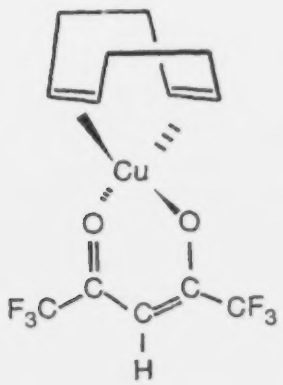
The TEDA and QUIN complexes with $Cr(acac)_3$ were not obtainable with our experimental conditions. A probable reason is that the same case as $Co(acac)_3 \cdot (TEDA)$ or $Co(acac)_3 \cdot (QUIN)$ was encountered here: the coordination sphere on the central chromium atom is full, and the TEDA/QUIN molecule is unable to displace any of the acetylacetonato ligands.

5.3 PREPARATION AND PHYSICAL DATA OF OTHER COMPLEXES

5.3.1 Copper Complexes

The preparation of $Cu(hfac) \cdot (1,5\text{-COD})$ was straightforward as described in Ref 23. The yield, as indicated in Table 3, was greater than 100%. This was attributed to impurities, or possible byproducts such as $Cu(hfac)_2 \cdot (1,5\text{-COD})$ or $Cu(hfac) \cdot 2(1,5\text{-COD})$.

Cu(1,5-COD)hfac



The FTIR spectrum of this complex is shown in Figure 31, and the ^1H NMR spectrum in Figure 32. The FTIR spectrum of Cu(hfac)·(1,5-COD) appeared the same when it was fresh (from synthesis) or exposed to air for 16 hours. However, after a few days, this compound turned to a greenish colour (probably indicating some decomposition). The ^1H NMR spectrum revealed resonances at 2.4 ppm ($-CH_2$ of 1,5-COD), 5.5 ppm (-CH of 1,5-COD) and 5.9 ppm (=CH of hfac). The identification of these resonances was based on: (i) the resonances at 2.4 and 5.5 ppm are similar to those previously observed for 1,5-COD (35), and (ii) a neat sample of hexafluoroacetylacetone has resonance at 6.4 ppm. The 5.9 ppm resonance observed in Figure 32 is probably due to an upfield shift (less deshielding) because the hexafluoroacetylacetone is now bonded to the central copper metal ion. Thus the characterization of this complex, Cu(hfac)·(1,5-COD) is quite complete.

Using the same preparative procedure as Cu(hfac)·(1,5-COD), Cu(hfac)(1,3-CHD) was synthesized. However, no characterization on this complex was made because this complex is air sensitive.

There was no literature reference on the preparation of the complex, $Cu(dmg)_2$·(TEDA). A 1:1 molar addition of $Cu(dmg)_2$ to TEDA yielded a brownish precipitate. The characterization was based on FTIR spectroscopy. The FTIR spectrum of $Cu(dmg)_2$·(TEDA) (Figure 33) differs significantly from the FTIR spectrum of $Cu(dmg)_2$ (shown in Figure 12) at 1550 cm^{-1} and in the fingerprint region from 500 to 1100 cm^{-1}. The UV/VIS spectrum of the complex $Cu(dmg)_2$·(TEDA) is shown in Figure 35. The λ_{max} were observed at 230 and 276 nm respectively. No UV/VIS spectrum was obtained for $Cu(dmg)_2$ because no suitable solvent was found for this compound.

P143922.PDF [Page: 38 of 81]

5.3.2 Cobalt Complexes

The attempt to synthesize the three complexes, Co(hfac)·(1,5-COD), $Co(acac)_2$·(1,5-COD) and $Co(acac)_3$·(1,5-COD) were unsuccessful. It appeared that the 1:1 addition of $Co(acac)_2$ or $Co(hfac)_2$ to 1,5-cyclooctadiene would not yield the desired product. Furthermore, from the synthesis of Cu(hfac)·(1,5-COD) (discussed in Section 5.3.1) it may seem that the starting material of the central metal atom, Cu_2O in this case, is required to be of lower oxidation state than the finished product. However a similar reaction in the preparation of Cu(hfac)·(1,5-COD) starting with CuCl was unsuccessful. Thus this reaction may be more complicated than is reported here or in Ref 23.

5.3.3 Silver Complexes

Two complexes, Ag(hfac)·(1,5-COD), and Ag(hfac)·(1,4-CHD) had been synthesized according to procedure given in Ref 33. Both complexes were brown precipitates, with very similar melting points, FTIR and ^1H NMR spectra. The FTIR spectra for both silver complexes are very similar to those observed for Cu(hfac)·(1,5-COD) and Cu(hfac)·(1,3-CHD).

The ^1H NMR spectrum of Ag(hfac)·(1,5-COD) shows resonances at 2.5, 5.8 and 6.1 ppm respectively, very similar to those observed previously for Cu(hfac)·(1,5-COD). The same applied to the ^1H NMR spectrum of Ag(hfac)·(1,3-CHD).

6.0 CONCLUSIONS

This report describes the ground work in the procurement, syntheses and the physical data of some organometallic complexes containing transition metals such as copper, cobalt, chromium and silver. All of these metals except cobalt have been used as impregnants to increase the chemical activity of activated carbon. In this initial attempt, only three classes of complexes, i.e. (i) metal salts + TEDA (or QUIN); (ii) metal + acetylacetone (or hexafluoroacetylacetone) + TEDA (or QUIN); and (iii) metal + hexafluoroacetylacetone + cyclic dienes were studied. Out of many attempted syntheses, only eighteen were successful. However, only a few of these will be assayed as impregnants on the activated carbon to enhance the carbon's chemical activity. There are several reasons for this, such as (i) difficulty in preparation or the low yield of the complexes; (ii) the difficulty of procurement of the starting materials, and (iii) no suitable carrier (e.g. solvent) to impregnate these transition metal complexes onto the carbon surface.

In a forth-coming report, these complexes will be impregnated on the activated carbon, and their performance against various toxic chemical warfare agents will be discussed.

7.0 REFERENCES

1. R.J. Grabenstetter and F.E. Blancet, Summary Technical Report of Division 10, National Defence Research Committee, Volume 1 - Military Problems with Aerosols and Non-Persistent Gases. Chapter 4 - Impregnation of Charcoal (1946).

2. S.H.C. Liang, B.H. Harrison, R.T. Poirier, B. Zanette and J.G. Pagotto. DREO Report No. 983 (1988).

3. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry. A Comprehensive Text. Part III Chemistry of Transition Elements, pp 619-1005 Wiley-Interscience Publication (4th Edition (1980)).

4. J.L. Hammarstrom and A. Sacco Jr. J. Catal. 112, 267-281 (1988).

5. J. Hanika, V. Machek, V. Nemec, V. Ruzicka and J. Kunz, J. Catal 77, 248 (1982).

6. See, for example: (a) I. Rodriguez-Ramos, J. Guerrera-Ruiz and J.L.G. Fierro, Appl. Surf Sci. 40, 239-247 (1989); (b) Yu. A. Ryndin, O.S. Alekseev, P.A. Simonov and V.A. Likholobov, J. Mol. Catal. 55, 109-125 (1989); (c) J.C. Menezo, L.C. Hoang, C. Montassier and J. Barbier, Appl. Catal. 74, L5-L10 (1991); (d) H.E. Van Dam and H. Van Bekkum, J. Catal. 131, 335-349 (1991).

7. G.J. Tennenhouse and J.C. Bailar, Jr., J. Inorg. Nucl. Chem., 28, 684 (1966).

8. H.M. Hilliard and J.T. Yoke III, Inorg. Chem., 5, 57 (1966).

9. E.D. Stevens and J.T. Yoke, Inorganica Chim. Acta., 4, 244 (1970).

10. H.M. Hilliard, D.D. Axtell, M.M. Gilbert and J.T. Yoke, J. Inorg. Nucl. Chem., 31, 2117 (1969).

11. P. Paoletti, J.H. Stern and A. Vacca, J. Phys. Chem., 69, 3762 (1965).

12. V.M. Rao, D.N. Sathyanarayana and H. Manohar, J. Chem. Soc. Dalton Trans., 2167 (1983).

13. M. Melnik, Coord. Chem. Rev., 42, 259 (1982).

14. J.V. Quagliano, A.K. Banerjee, V.L. Goedken and L.M. Vallarino, J. Amer. Chem. Soc., 92, 482 (1970).

15. R.C.E. Belford, D.E. Fenton and M.R. Truter, J. Chem. Soc. Dalton Trans., 2208 (1972).

16. L.M. Vallarino, V.L. Goedken and J.V. Quagliano, Inorg. Chem.,11, 1466 (1972).

17. I.G. Dance and T.R. Miller, Inorg. Chem., 13, 525, (1974).

18. D.M.L. Goodgame and G. Brun, Bull. Soc. Chim. France, 7, 2236 (1973).

19. G. Brun and G. Jourdan, C. R. Acad. Sc. Paris, Ser C, 279, 129 (1974).

20. W. Rudzinski, M. Shiro and Q. Fernando, Anal. Chem., 47, 1194 (1975).

21. G. Brun, C. R. Acad. Sc. Paris, Ser C, 281, 869 (1975).

22. M. Hanack, S. Deger and A. Lange, Coord. Chem. Rev., 83, 115 (1988).

23. T.V. Sirota, S. Ivanov, S.K. Yanielyan and A.B. Gagarina, Oxid. Commun., 11, 99 (1988).

24. D. Leussing, Inorg. Chem. 2, 77 (1963).

25. D.A. Baldwin and G.J. Leigh, J. Chem. Soc. A, 1431 (1968).

26. D.P Graddon, Coordination Chem. Rev. 4, 1 (1969).

27. R.C. Elder, Inorg. Chem. 7, 1117 (1968); ibid. 7, 2316 (1968).

28. W.D. Horrocks Jr., D.H. Templeton and A. Zalkin, Inorg. Chem. 7, 1552 (1968).

29. B.J. Hathaway and D.E. Billing, Coordination Chem. Rev. 5, 143 (1970).

30. R.L. Belford, A.E. Martell and M. Calvin, J. Inorg. Nucl.Chem., 2, 11 (1956).

31. J. Ashley-Smith, M. Green and F.G.A. Stone, J. Chem. Soc. Dalton. Trans. 1805 (1972).

32. G. Doyle, K.A. Eriksen and D. Van Engen, Organometallics, 4, 830 (1985).

33. W. Partenheimer and E.H. Johnson, Inorg. Chem., 11, 2840 (1972).

34. G.J. Tennenhouse, Ph.D. Dissertation, University of Illinois (1963).

35. C.J. Pouchert, The Aldrich Library of NMR Spectra, 2nd ed. Volumes 1 and 2 (1983).

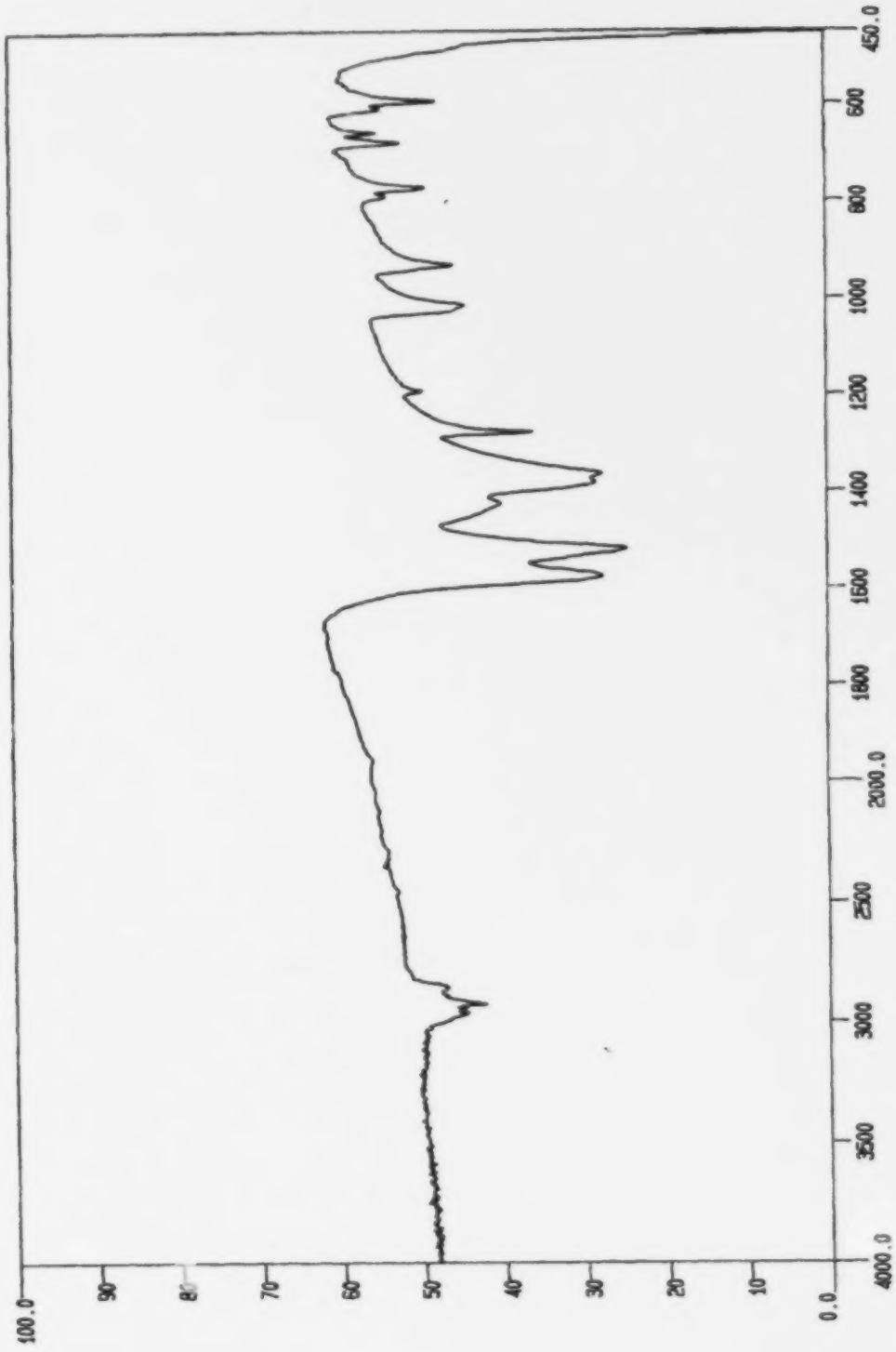


Figure 1: FTIR spectrum of $Cr(acac)_3$ in nujol.

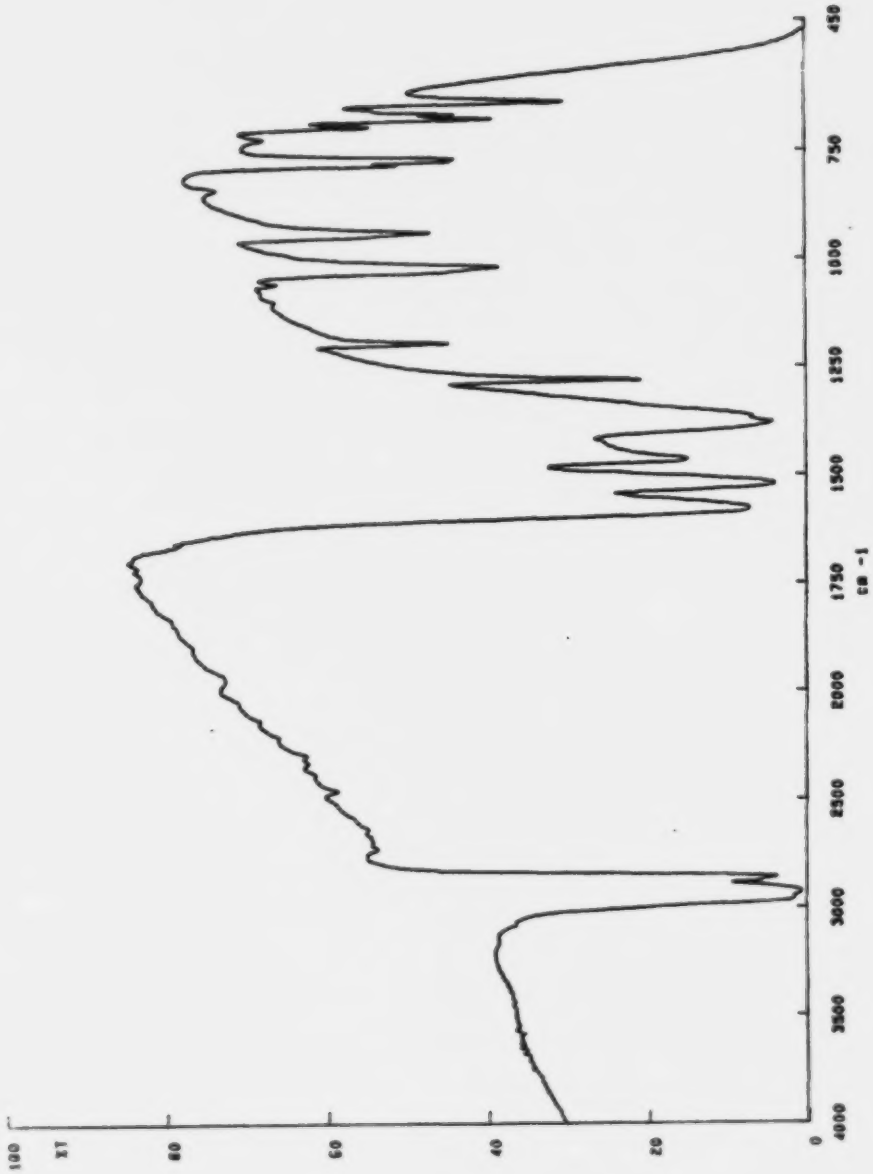


Figure 2: FTIR spectrum of $Co(acac)_3$ in nujol.

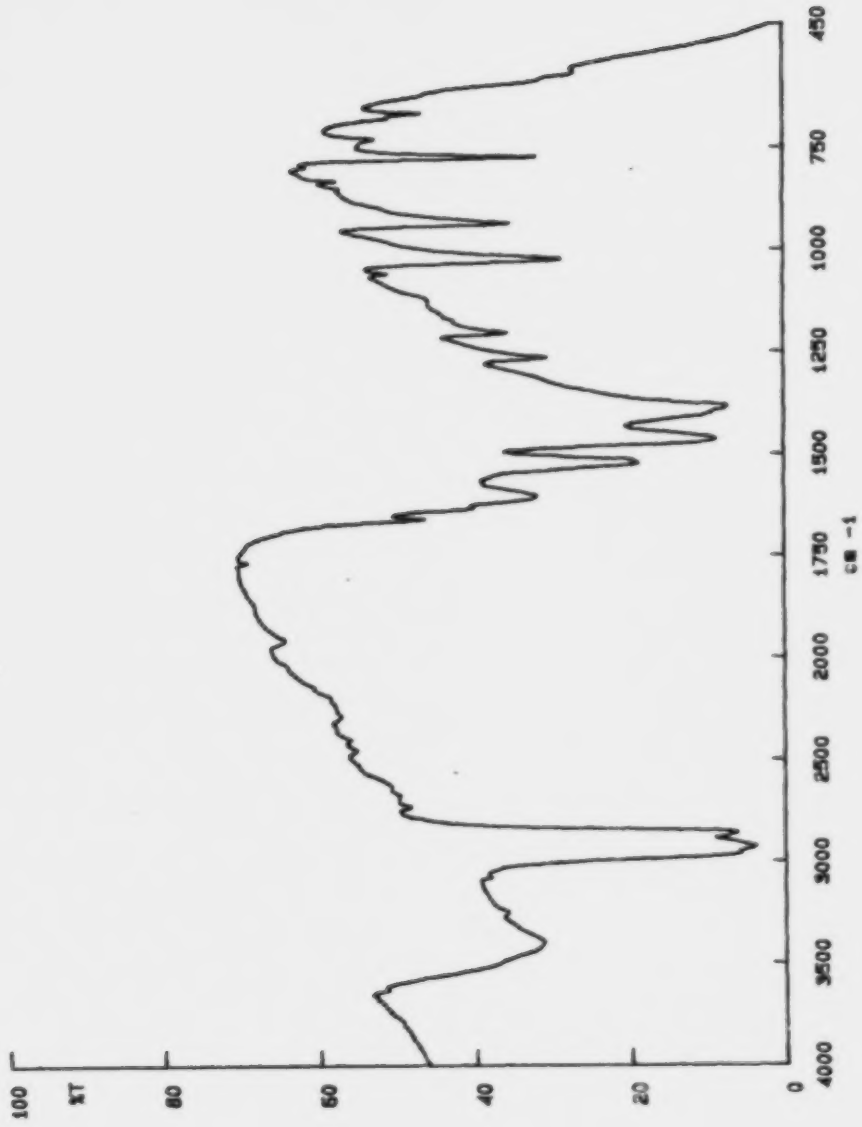


Figure 3: FTIR spectrum of $Co(acac)_2 \cdot H_2O$ in nujol.

P143922.PDF [Page: 45 of 81]

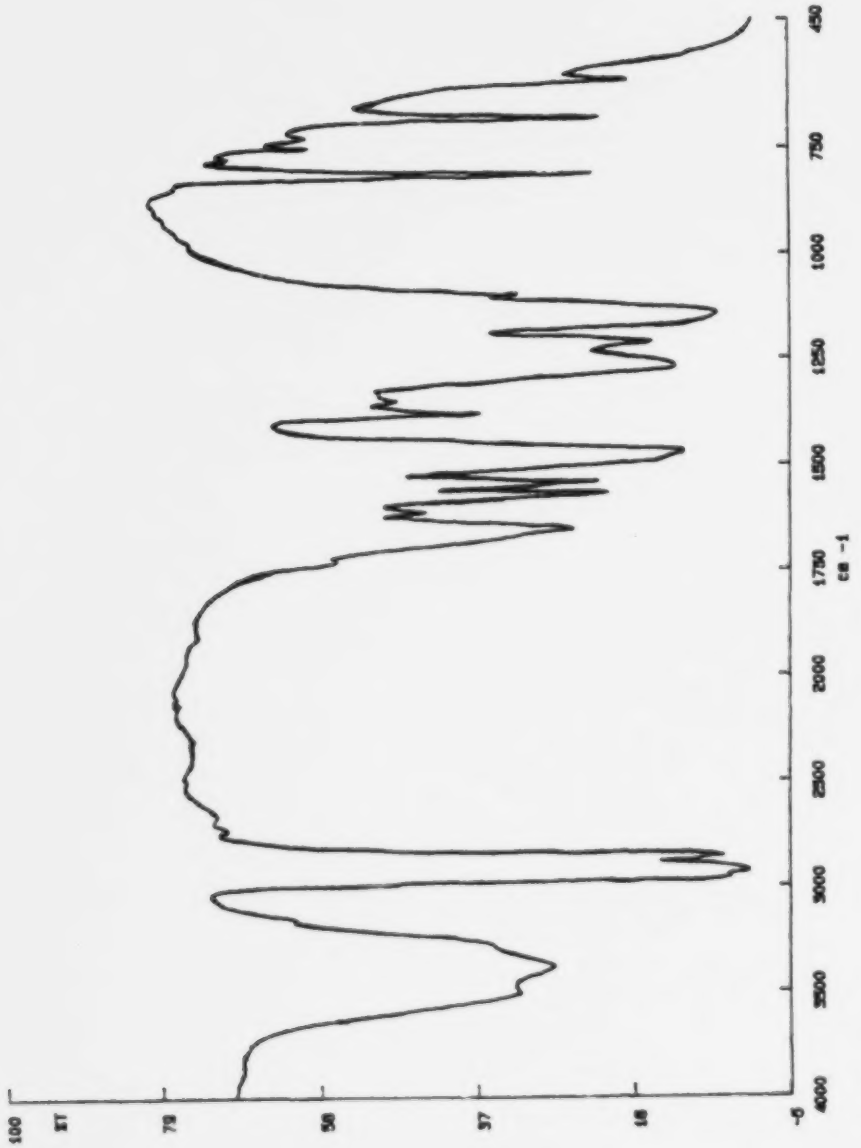


Figure 4: FTIR spectrum of $Co(hfac)_2 \cdot H_2O$ in nujol.

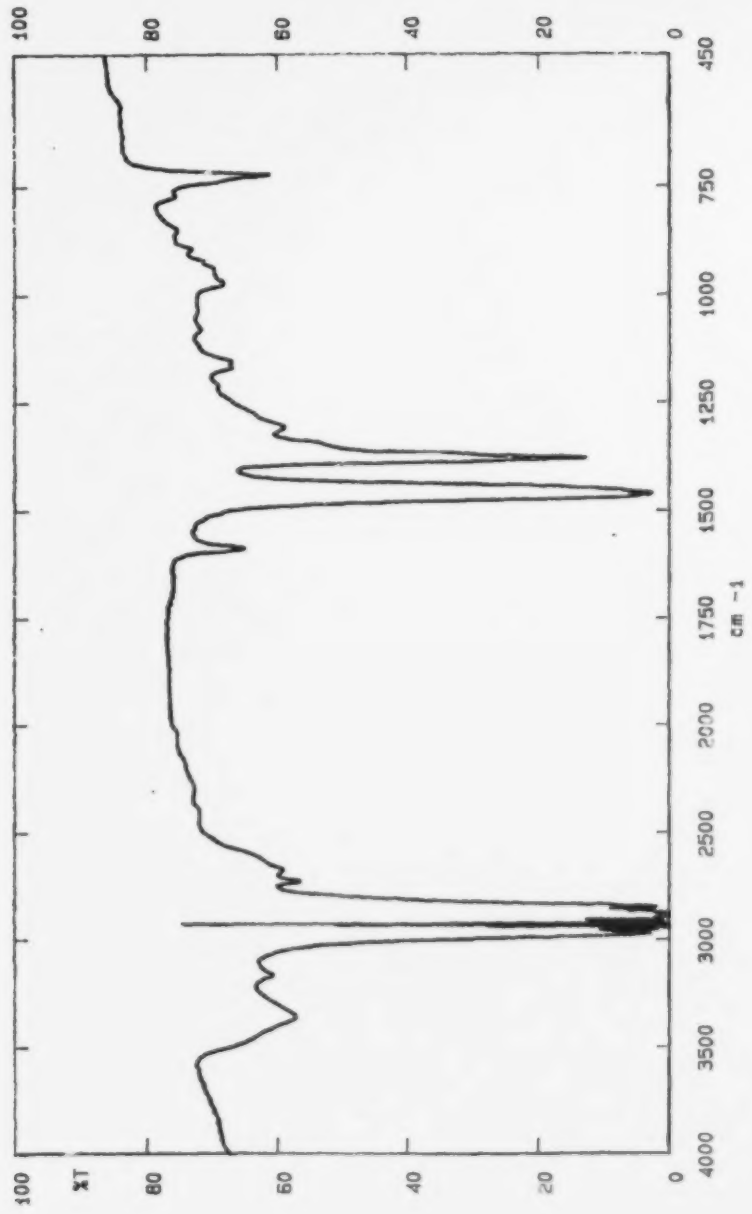


Figure 5: FTIR spectrum of $CuCl_2$ in nujol.

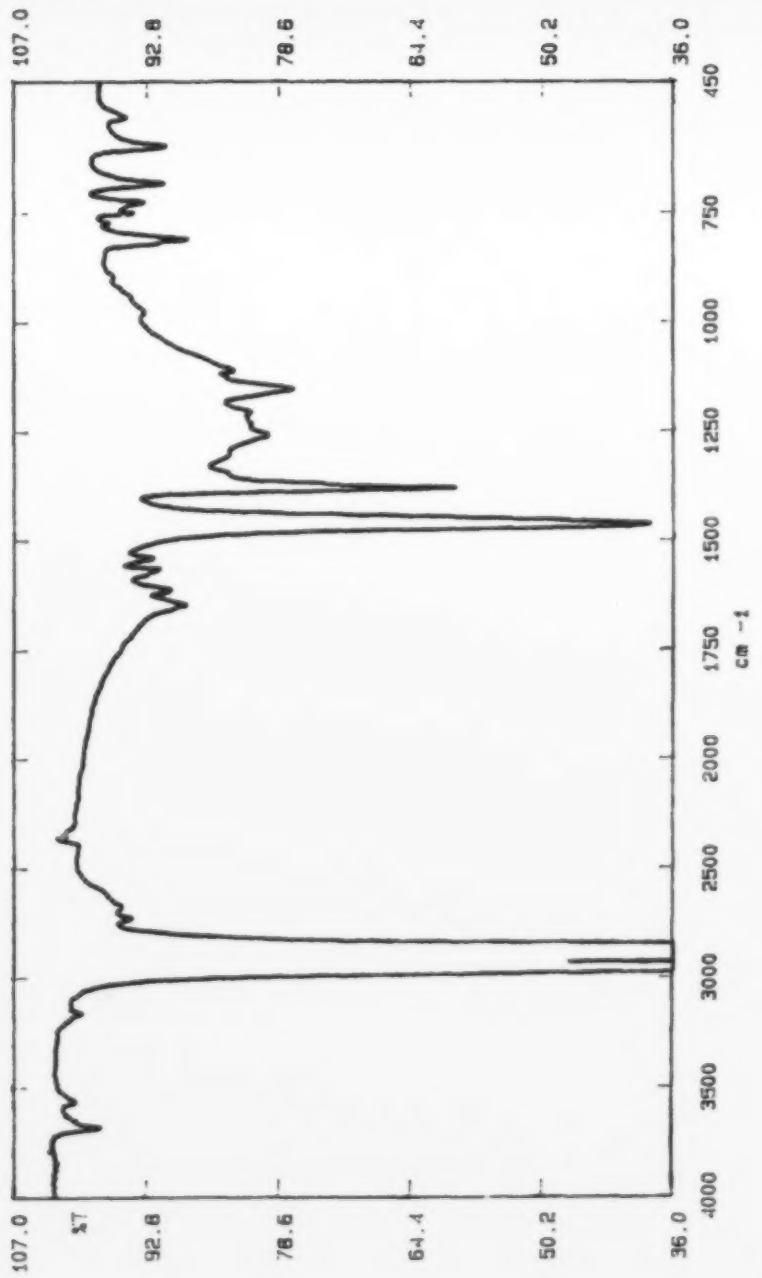


Figure 6: FTIR spectrum of $Cu(hfac)_2 \cdot H_2O$ in nujol.

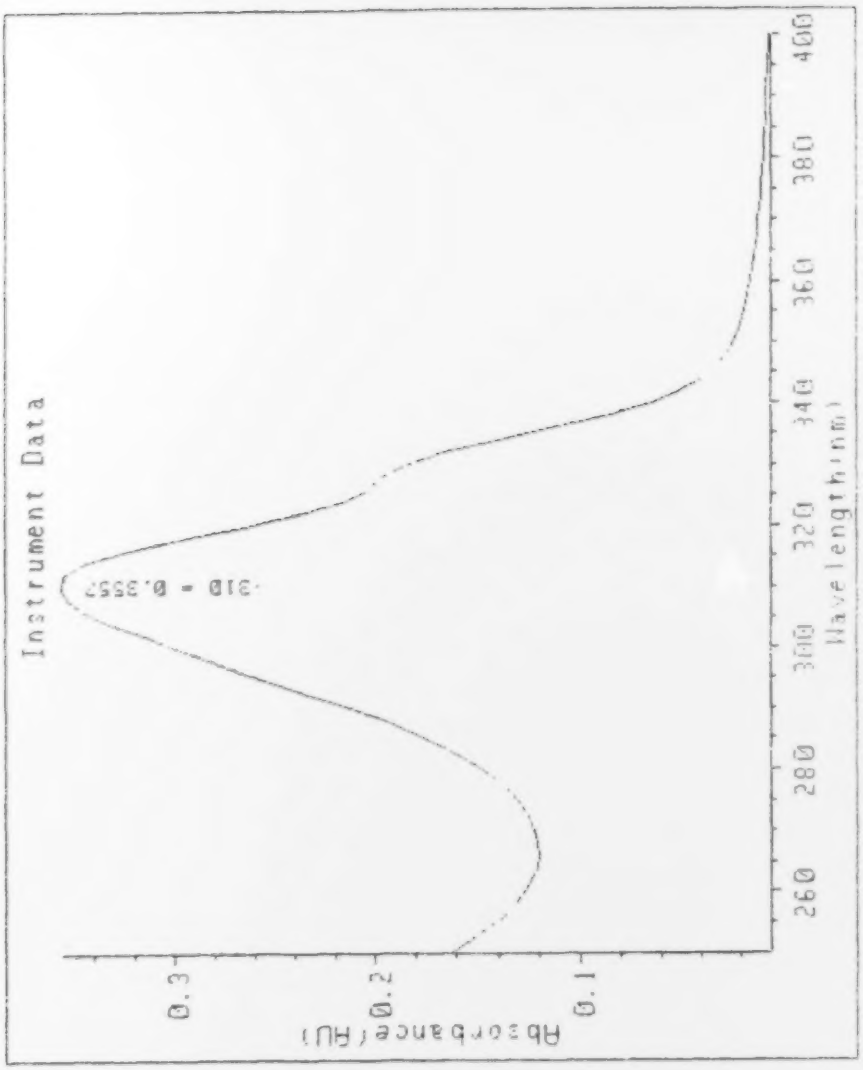


Figure 7: UV/VIS spectrum of $Cu(hfac)_2 \cdot H_2O$ in $CHCl_3$ from 240 to 400 nm (2×10^{-5} M).

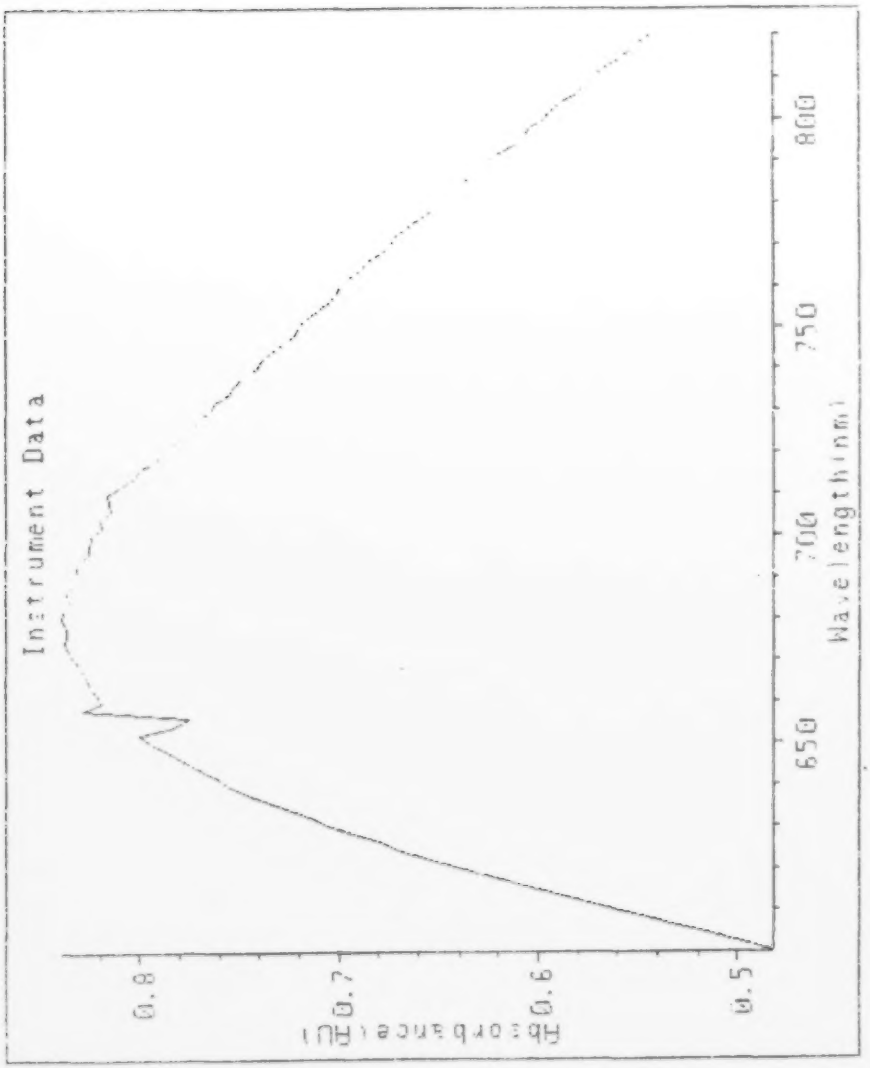


Figure 8: UV/VIS spectrum of $Cu(hfac)_2 \cdot H_2O$ in $CHCl_3$ from 600 to 820 nm (2.1×10^{-2} M).

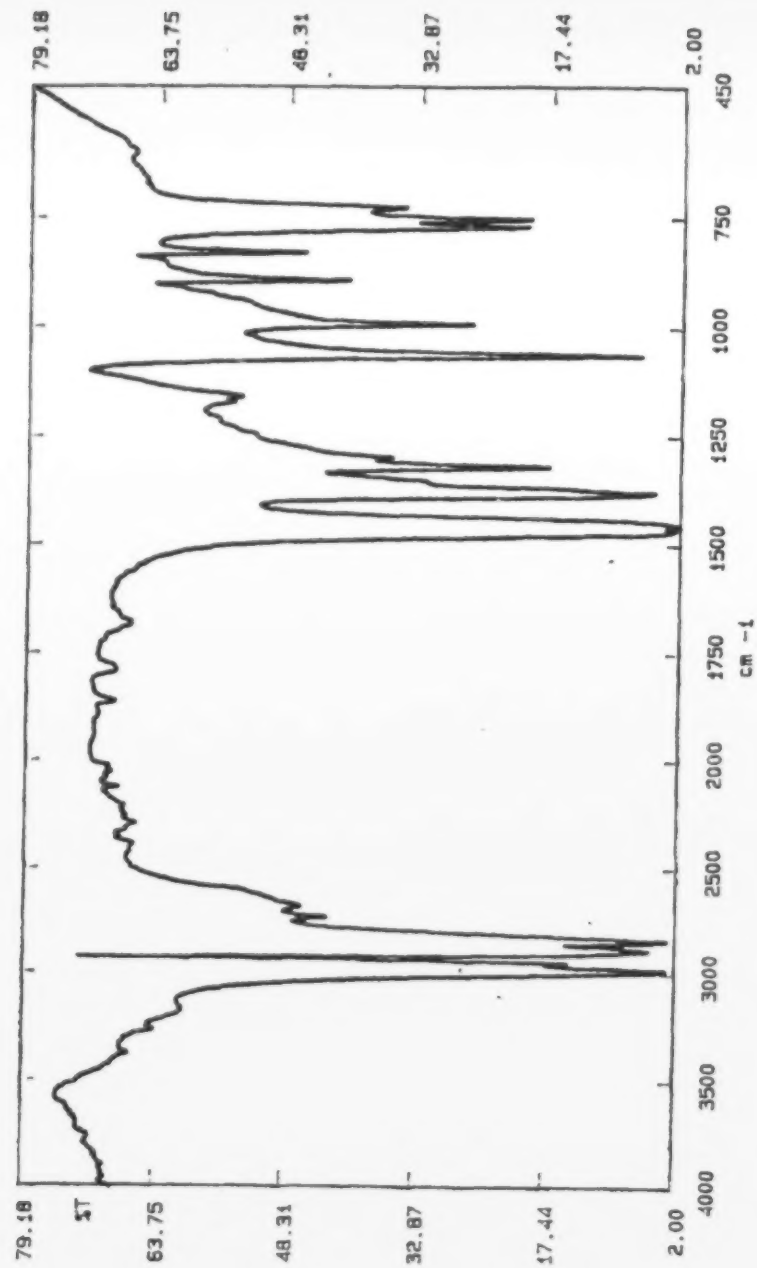


Figure 9: FTIR spectrum of triethylenediamine in nujol.

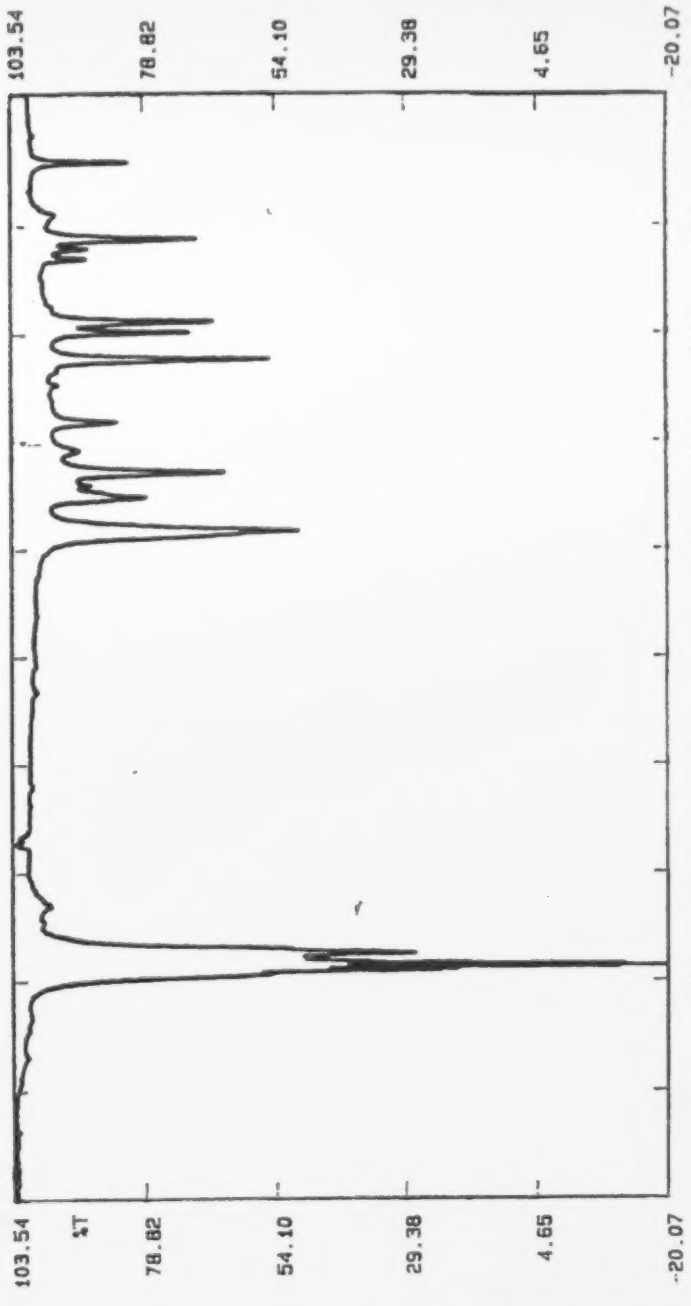


Figure 10: FTIR spectrum of quinuclidine in nujol

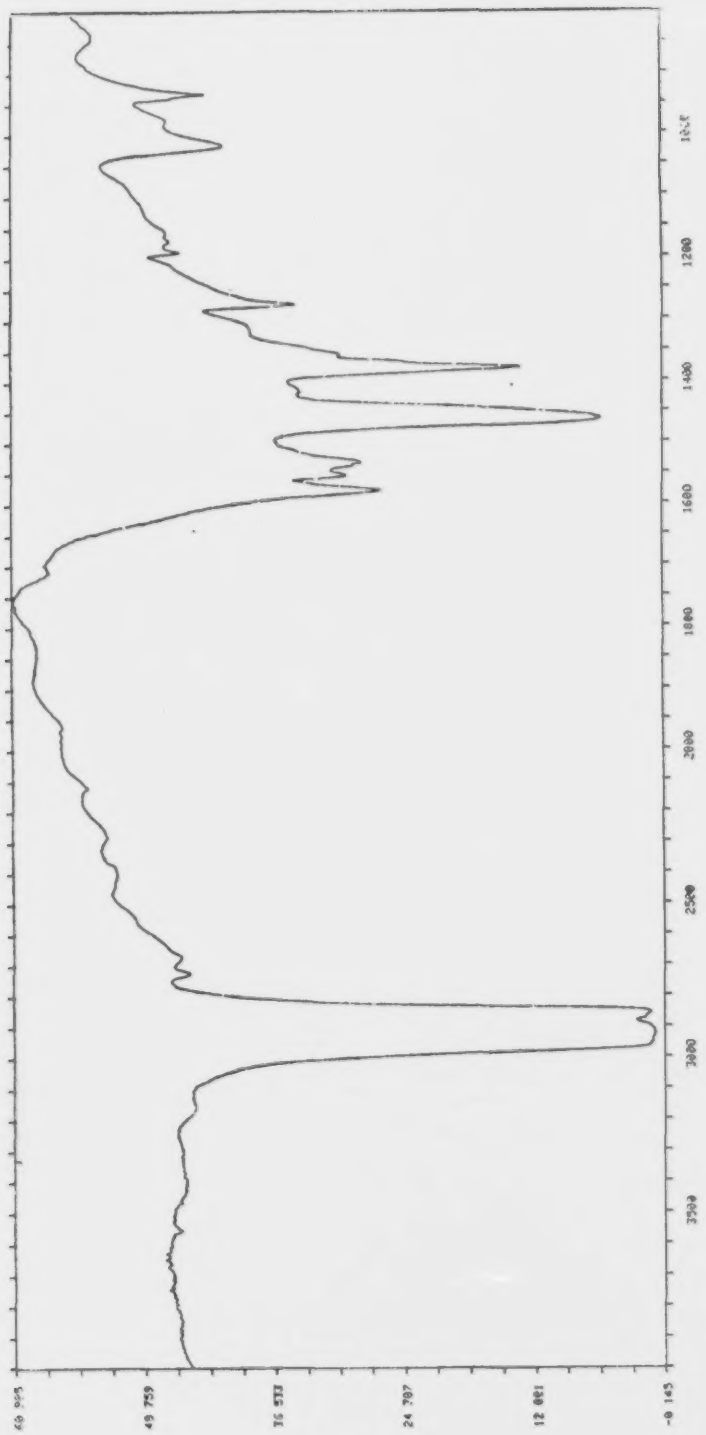


Figure 11: FTIR spectrum of $Cu(acac)_2$ in nujol.

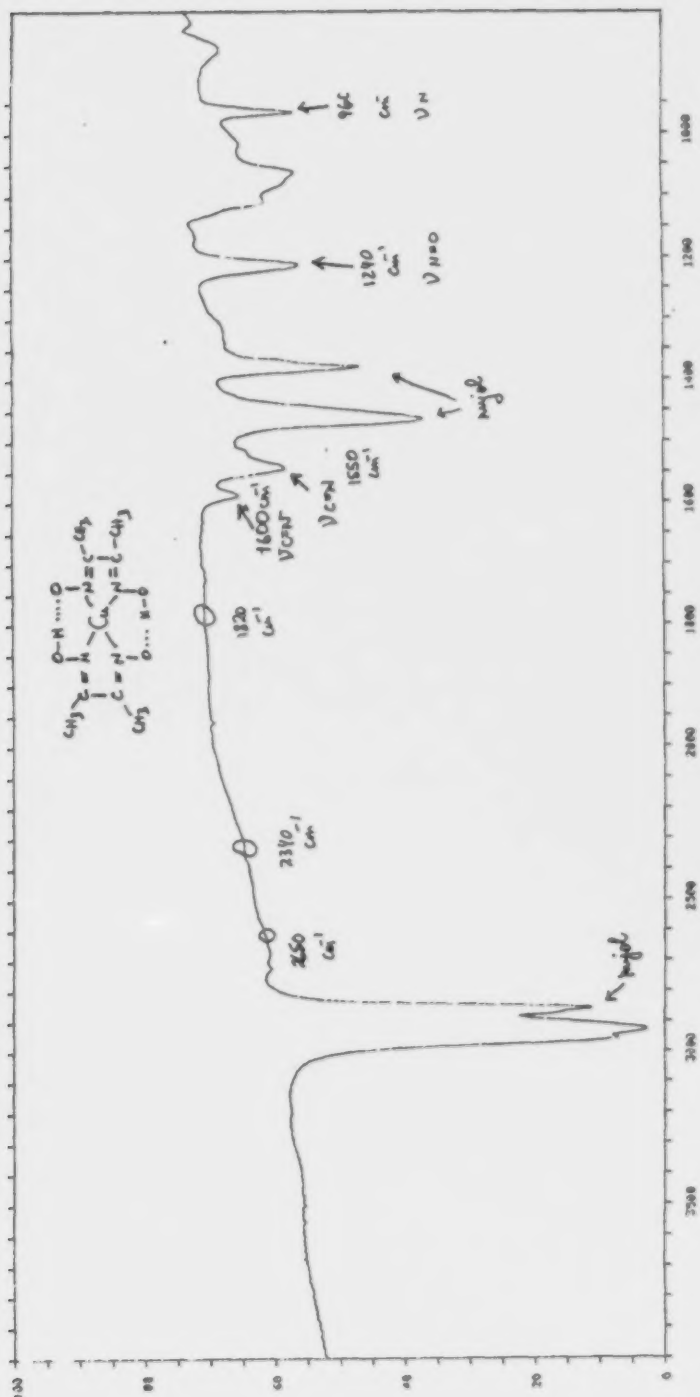


Figure 12: FTIR spectrum of bis(dimethylglyoximato)copper(II), $Cu(dmg)_2$ in nujol on ZnSe plates.

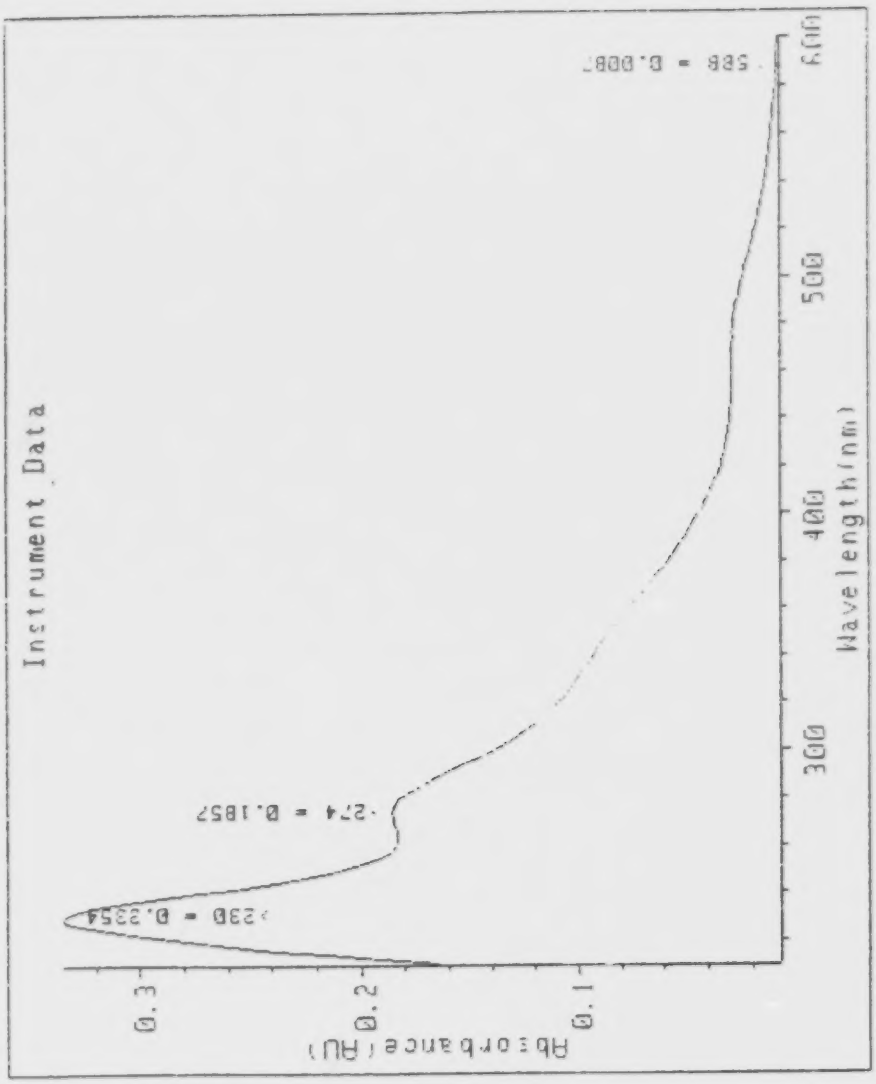


Figure 13: UV/VIS spectrum of $Cu(dmg)_2$ in ethanol (7×10^{-5} M).

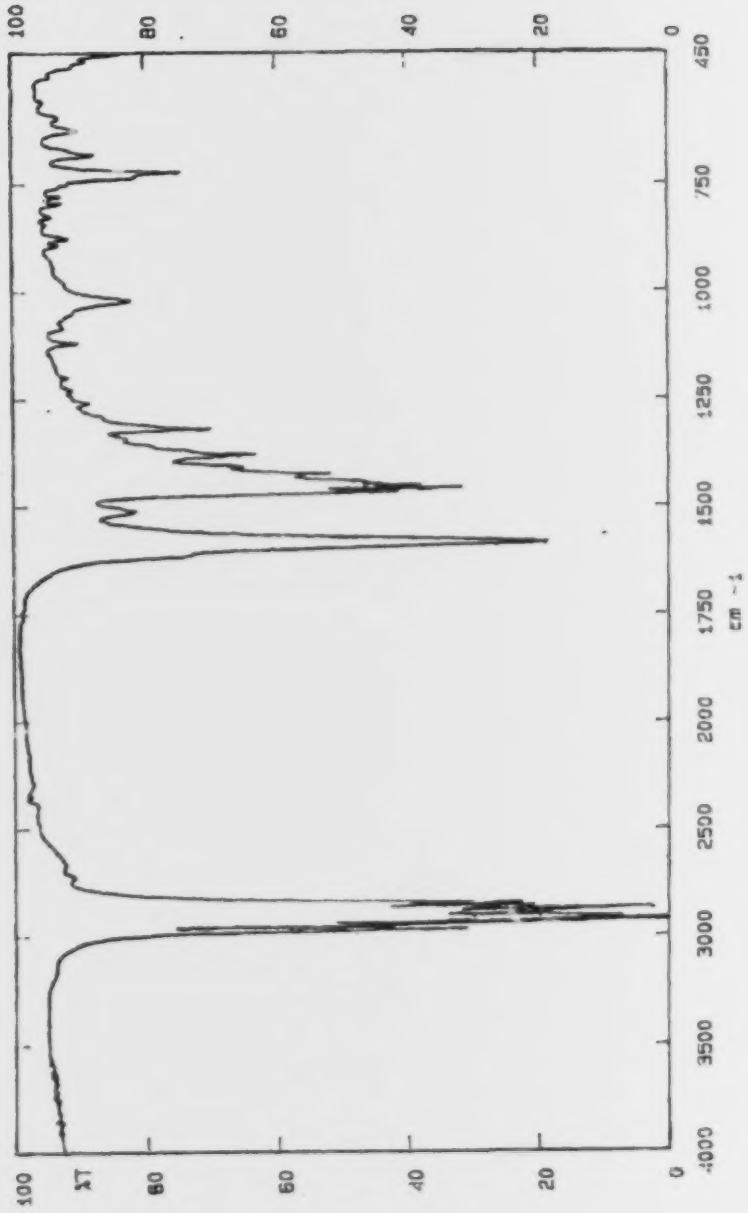


Figure 14: FTIR spectrum of Cu(laurate)$_2$ in nujol.

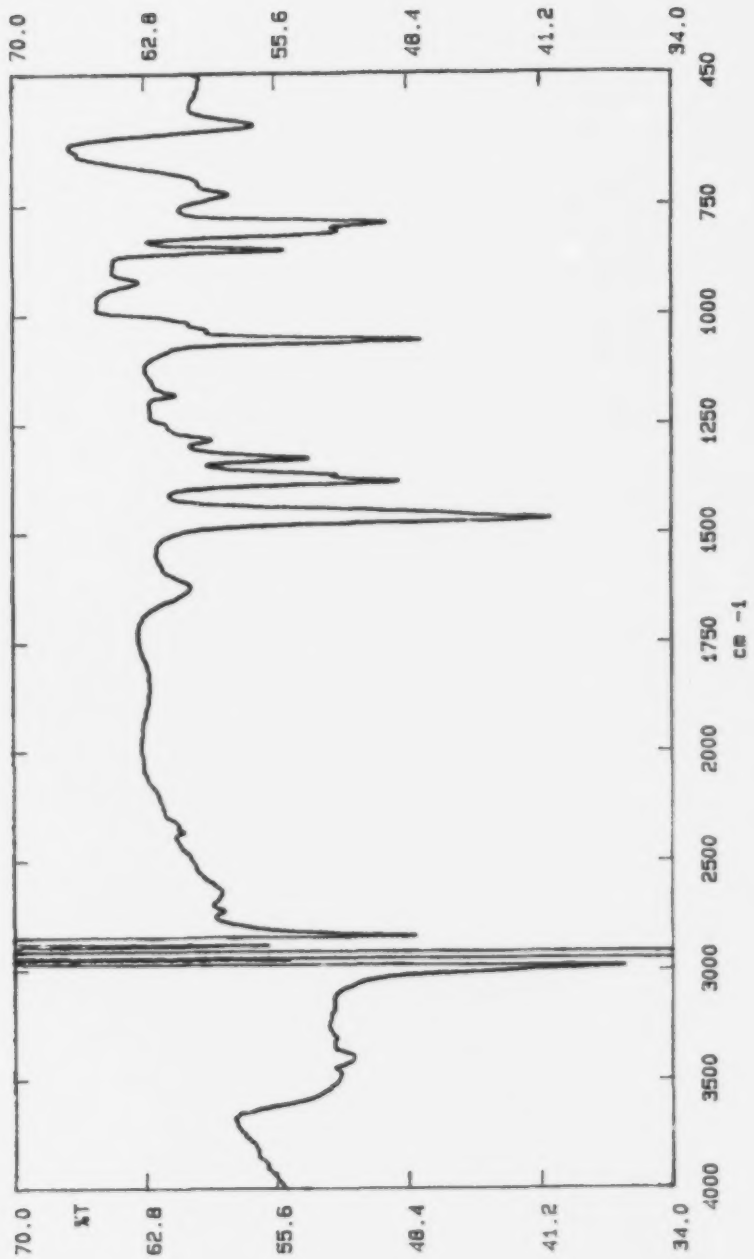


Figure 15: FTIR spectrum of $CuCl_2 \cdot (TEDA)$ in nujol.

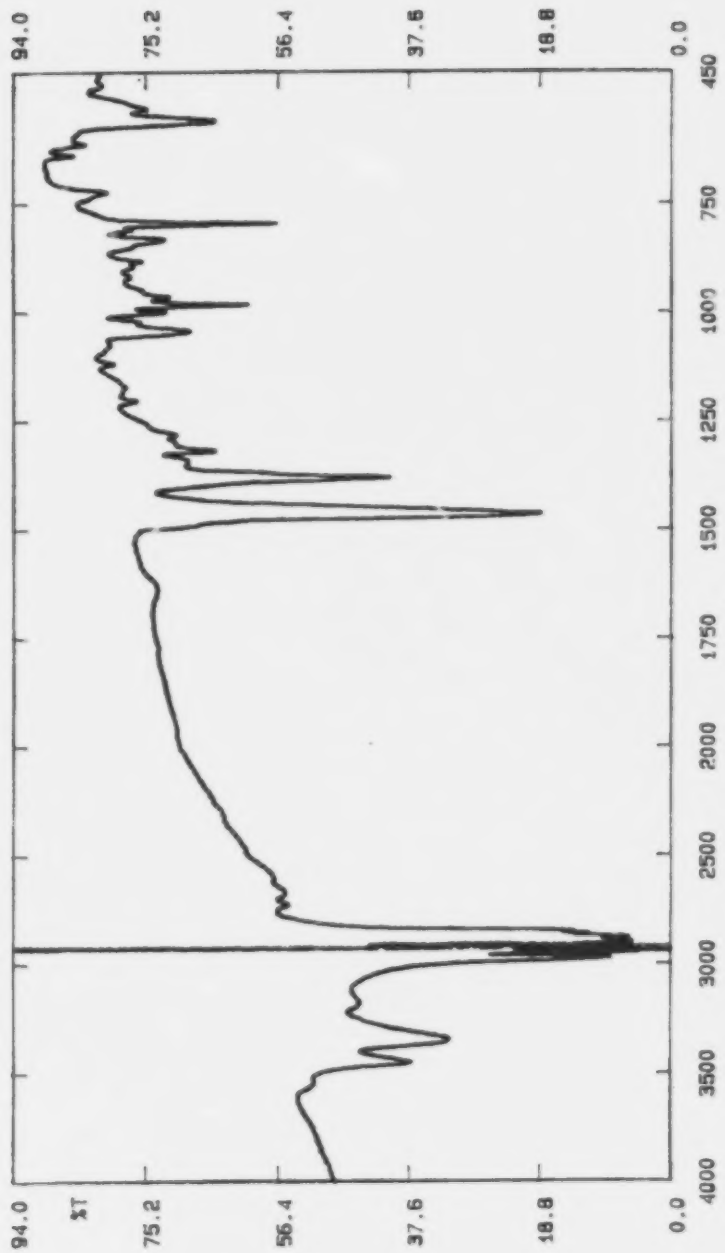


Figure 16: FTIR spectrum of $CuCl_2 \cdot (QUIN)$ in nujol.

P143922.PDF [Page: 58 of 81]

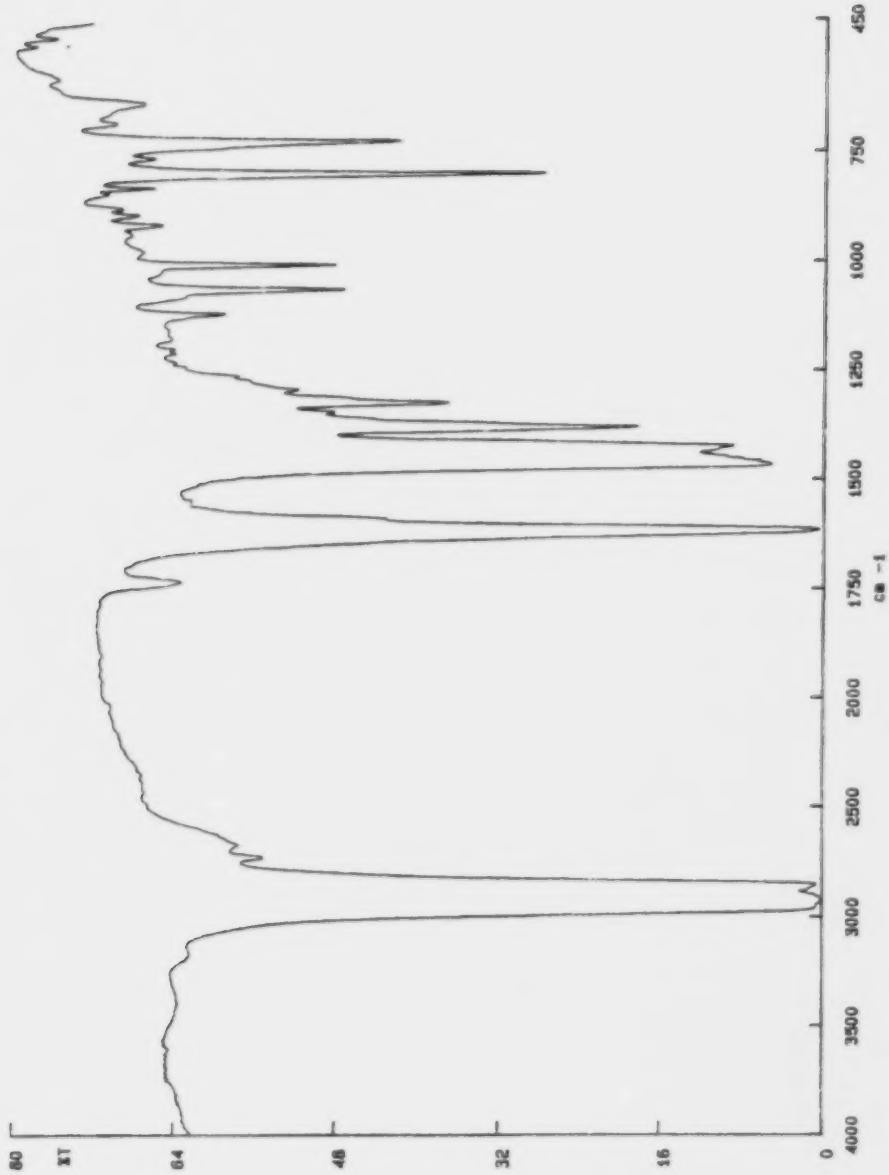


Figure 17: FTIR spectrum of Cu(laurate)$_2$·½(TEDA) in nujol.

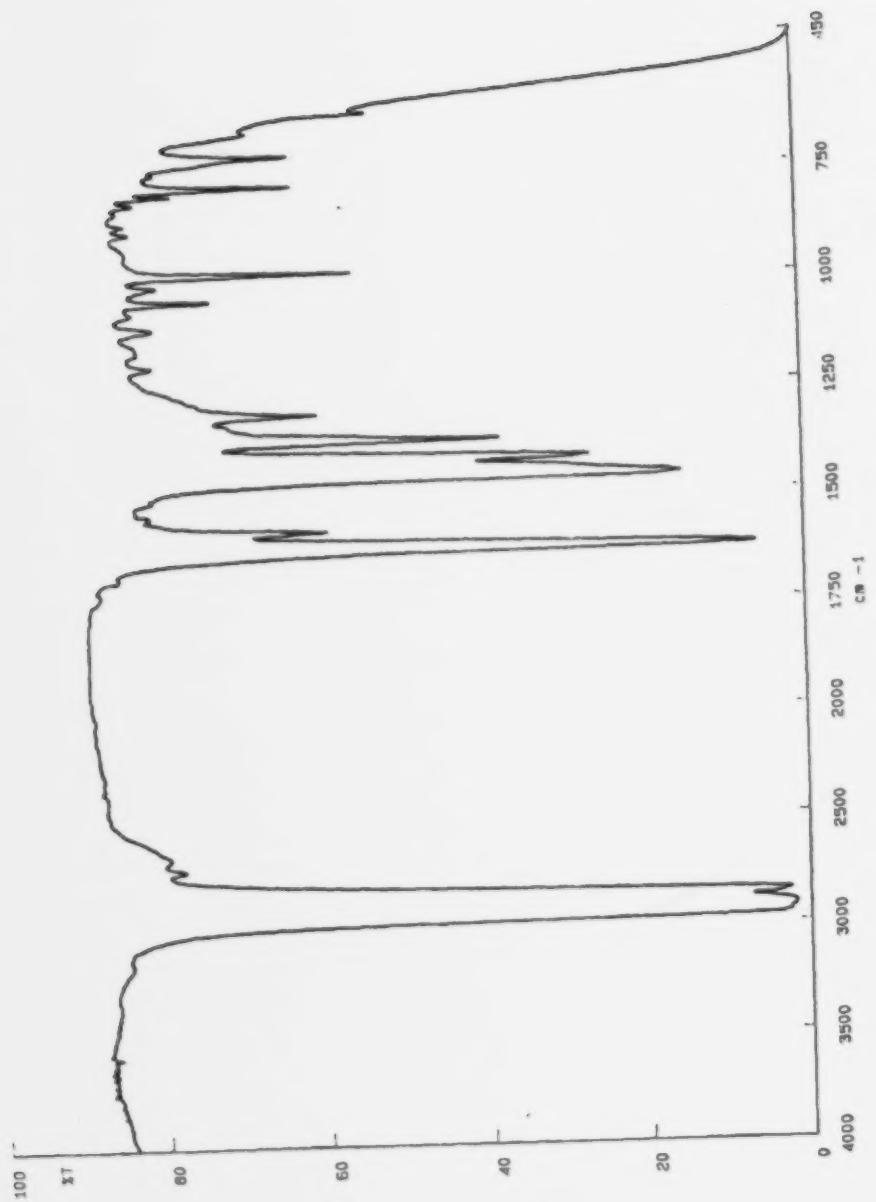


Figure 18: FTIR spectrum of Cu(laurate)$_2$·x(QUIN) in nujol.

P143922.PDF [Page: 60 of 81]

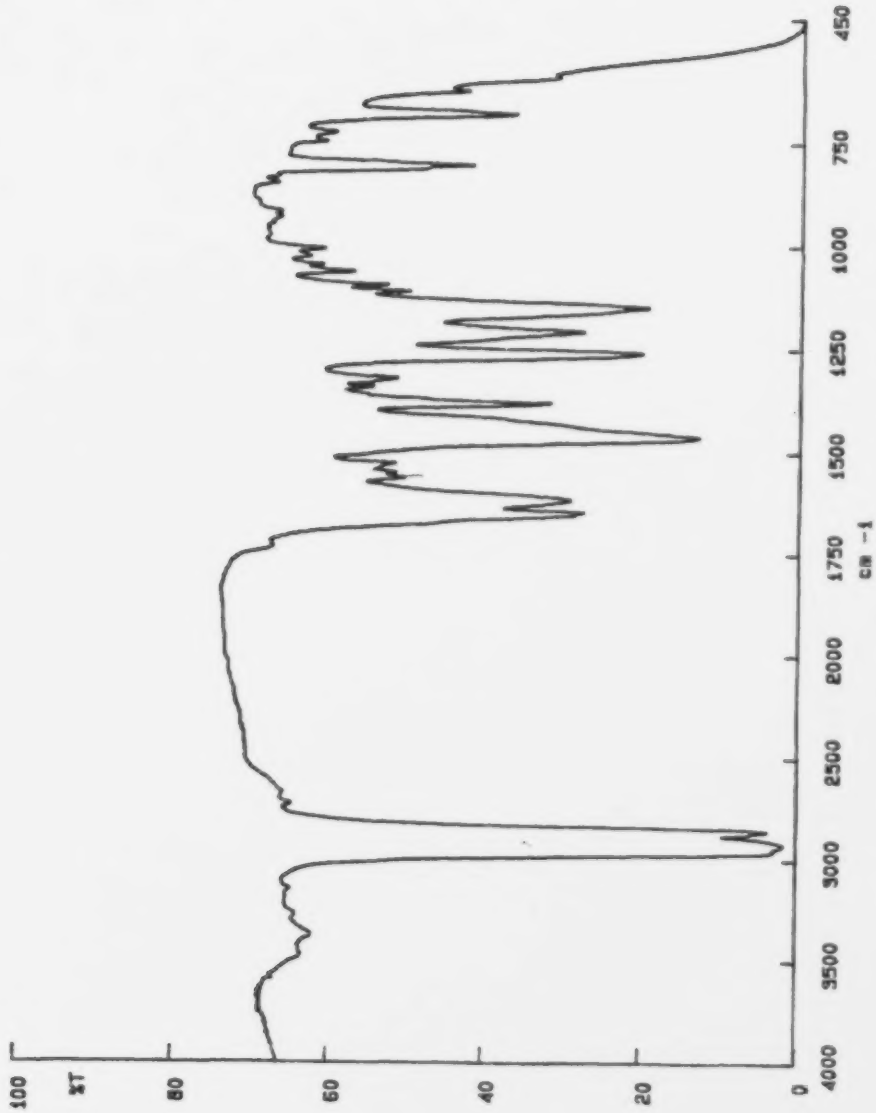


Figure 19: FTIR spectrum of $Cu(acetate)_2 \cdot \frac{1}{2}(TEDA)$ in nujol.

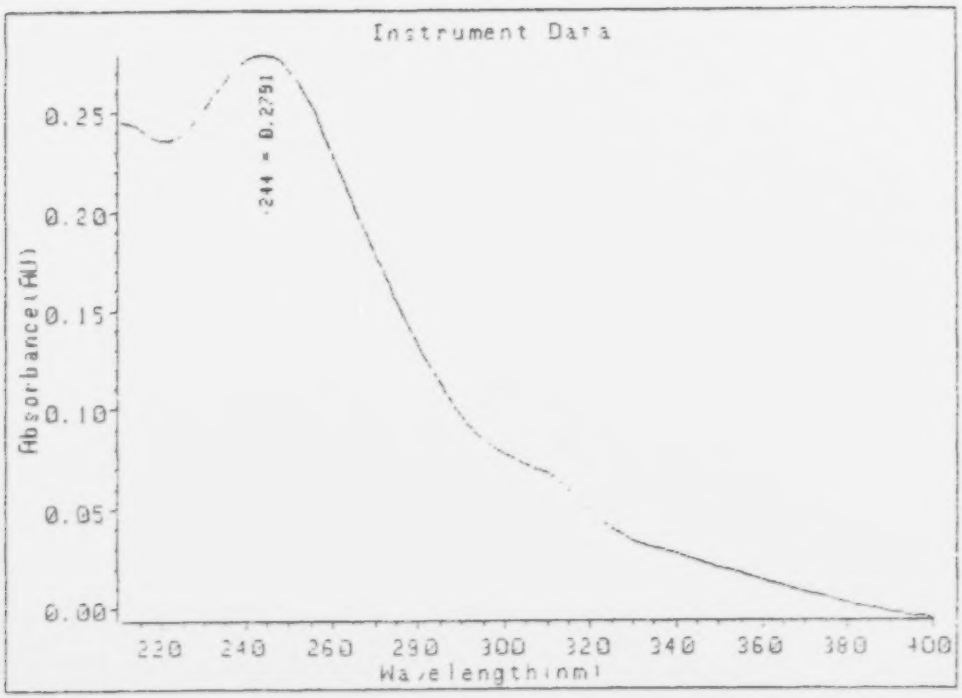


Figure 20: UV/VIS spectrum of $Cu(acetate)_2 \cdot \frac{1}{4}(TEDA)$ in methanol (1×10^{-4} M).

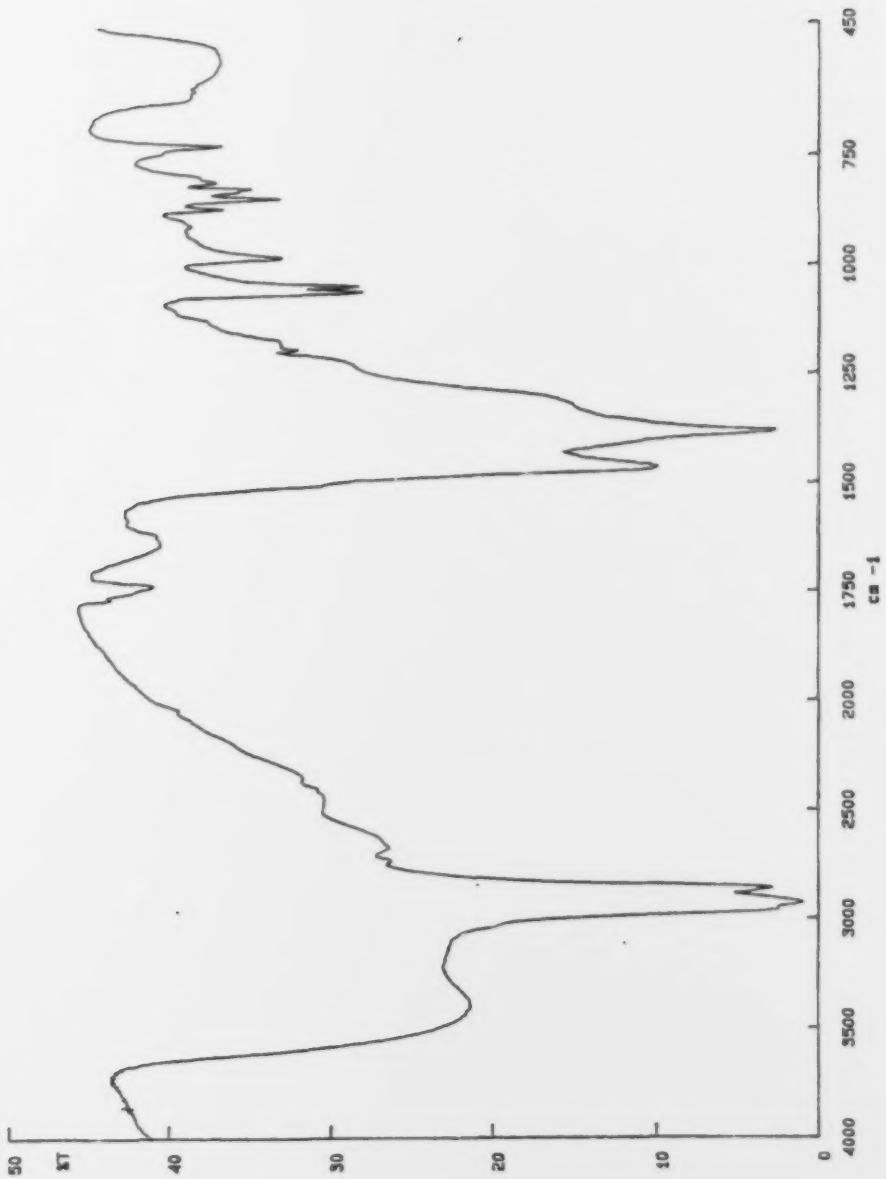


Figure 21: FTIR spectrum of $Cr(NO_3)_3 \cdot x(TEDA)$ in nujol.

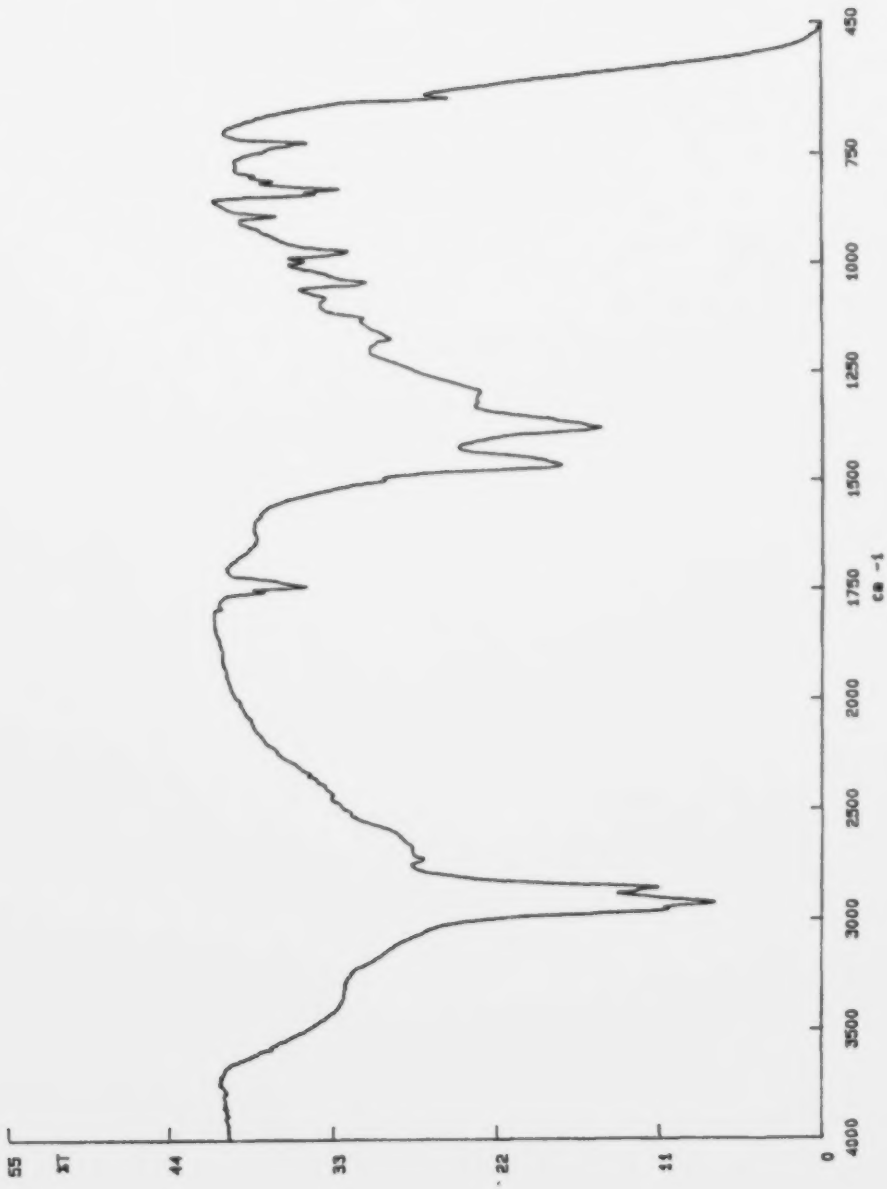


Figure 22: FTIR spectrum of $Cr(NO_3)_2 \cdot x(QUIN)$ in nujol.

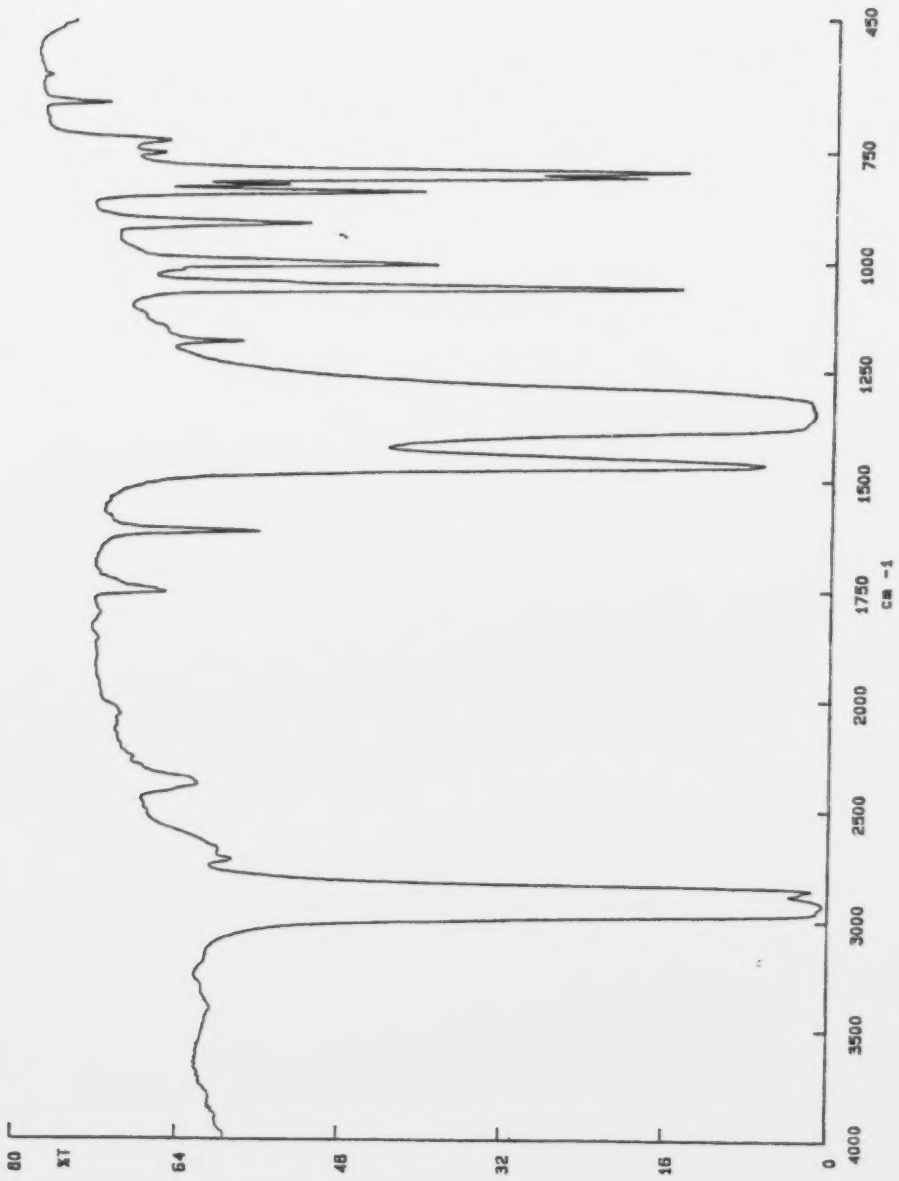


Figure 23: FTIR spectrum of $AgNO_3 \cdot x$(TEDA) in nujol.

P143922.PDF [Page: 65 of 81]

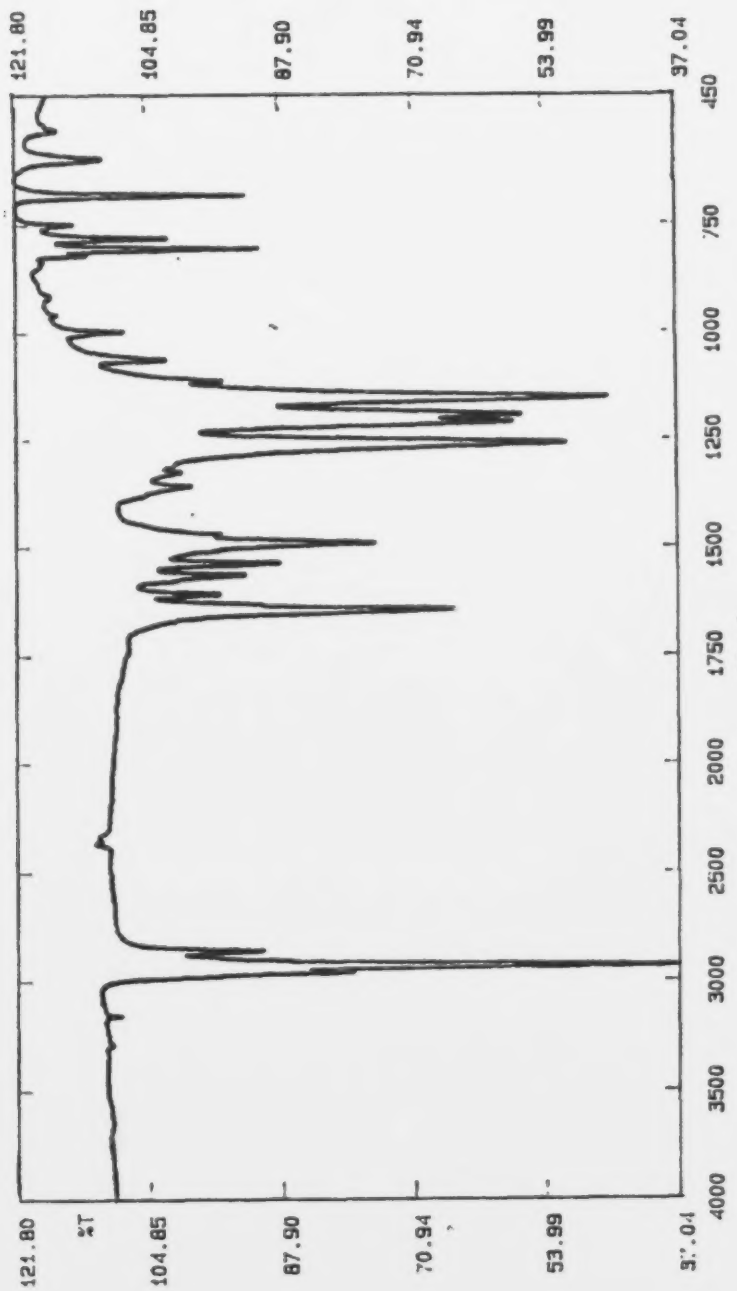


Figure 24: FTIR spectrum of $Cu(hfac)_2 \cdot (TEDA)$ in nujol.

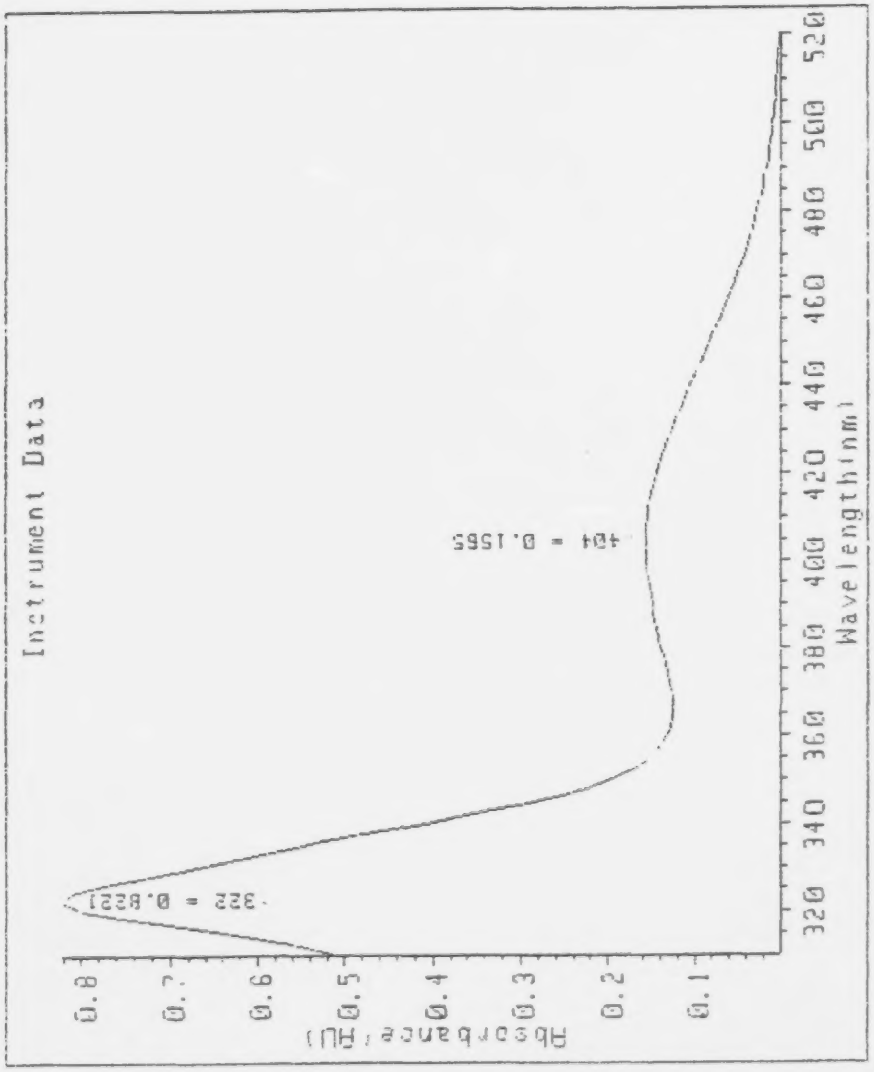


Figure 25: UV/VIS spectrum of $Cu(hfac)_2$·(TEDA) in CCl_4 (1.7×10^{-4} M) from 320 to 520 nm.

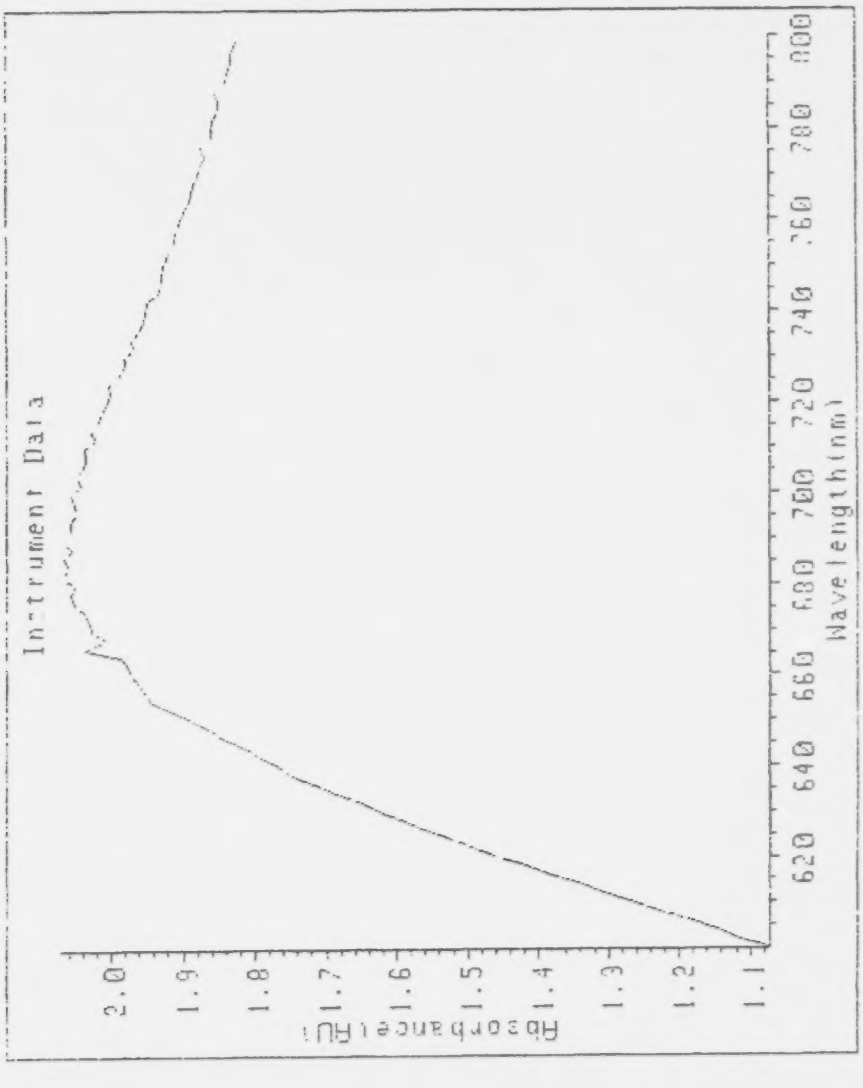


Figure 26: UV/VIS spectrum of $Cu(hfac)_2 \cdot (TEDA)$ in CCl_4 (1.7×10^{-2} M) from 600 to 800 nm.

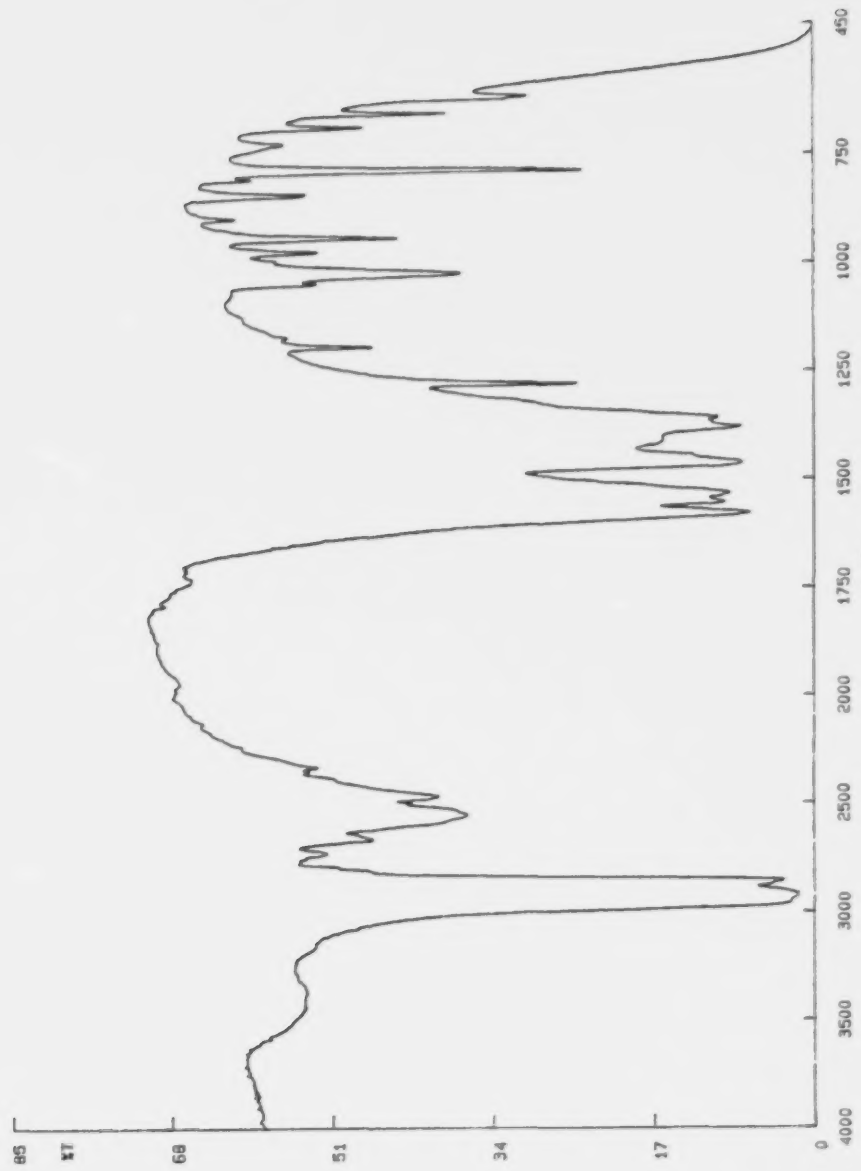


Figure 27: FTIR spectrum of $Cu(acac)_2 \cdot x(QUIN)$ in nujol.

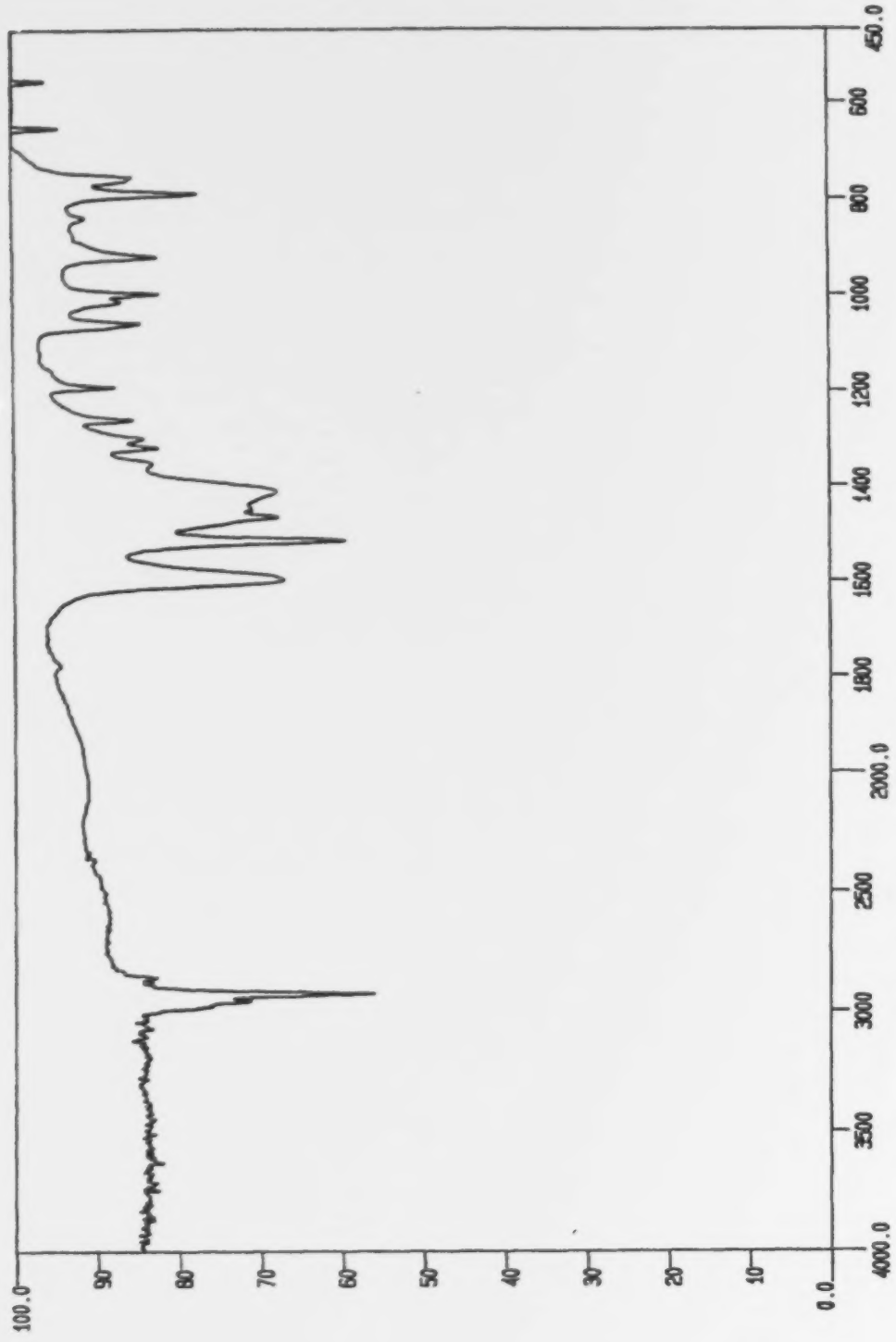


Figure 28: FTIR spectrum of $Co(acac)_2 \cdot x(TEDA)$ in nujol.

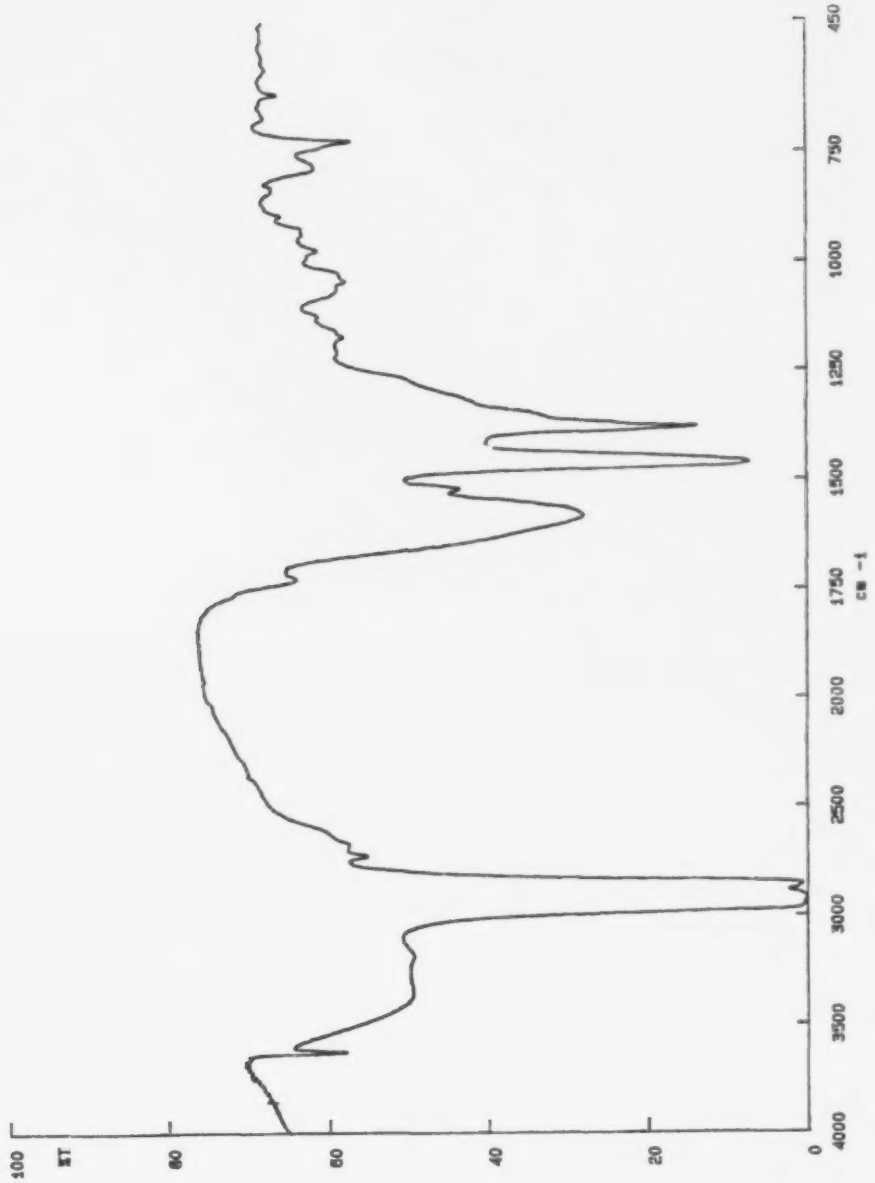


Figure 29: FTIR spectrum of $Co(acac)_2 \cdot (QUIN)$ in nujol.

P143922.PDF [Page: 71 of 81]

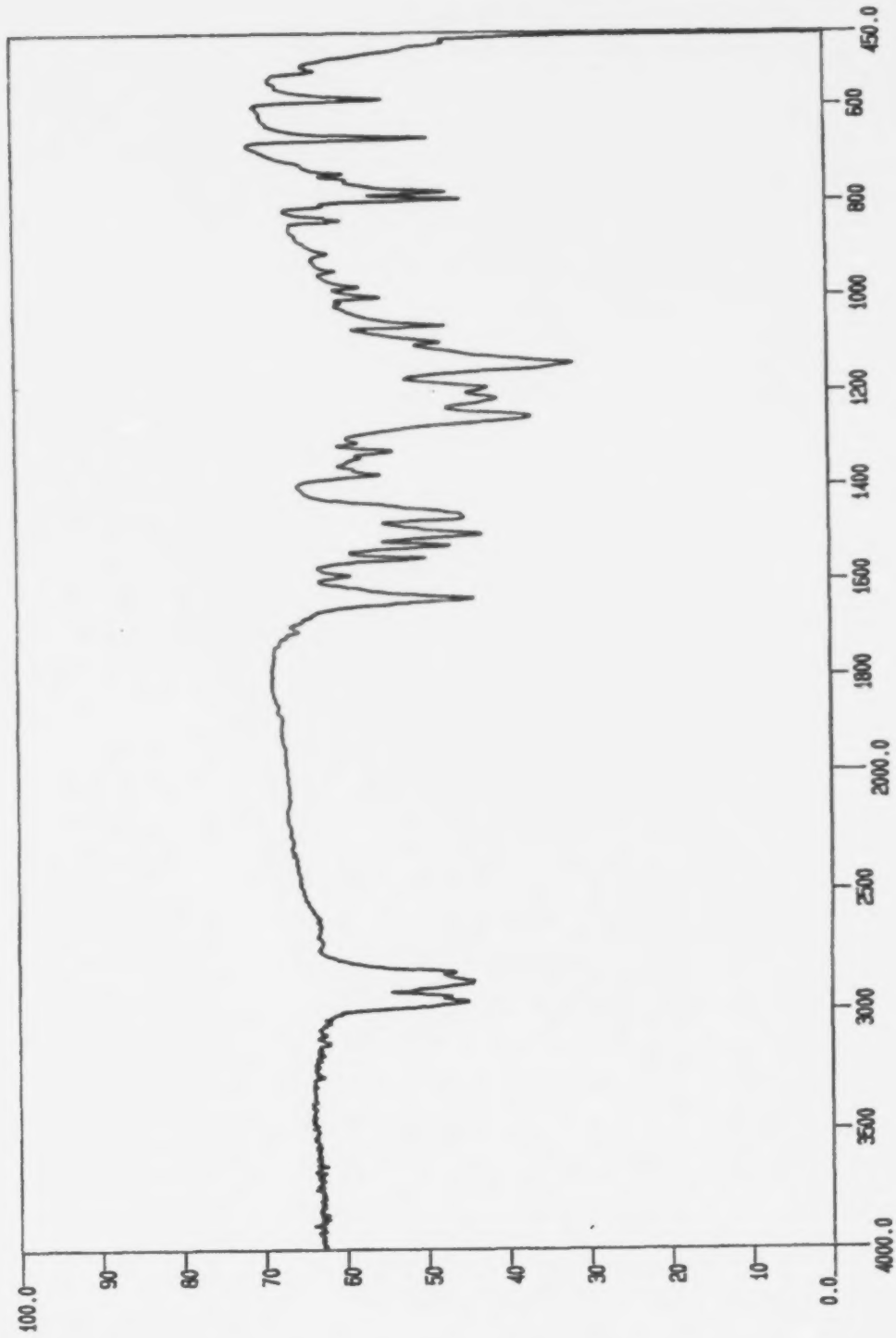


Figure 30: FTIR spectrum of $Co(hfac)_2 \cdot 2(TEDA)$ in nujol.

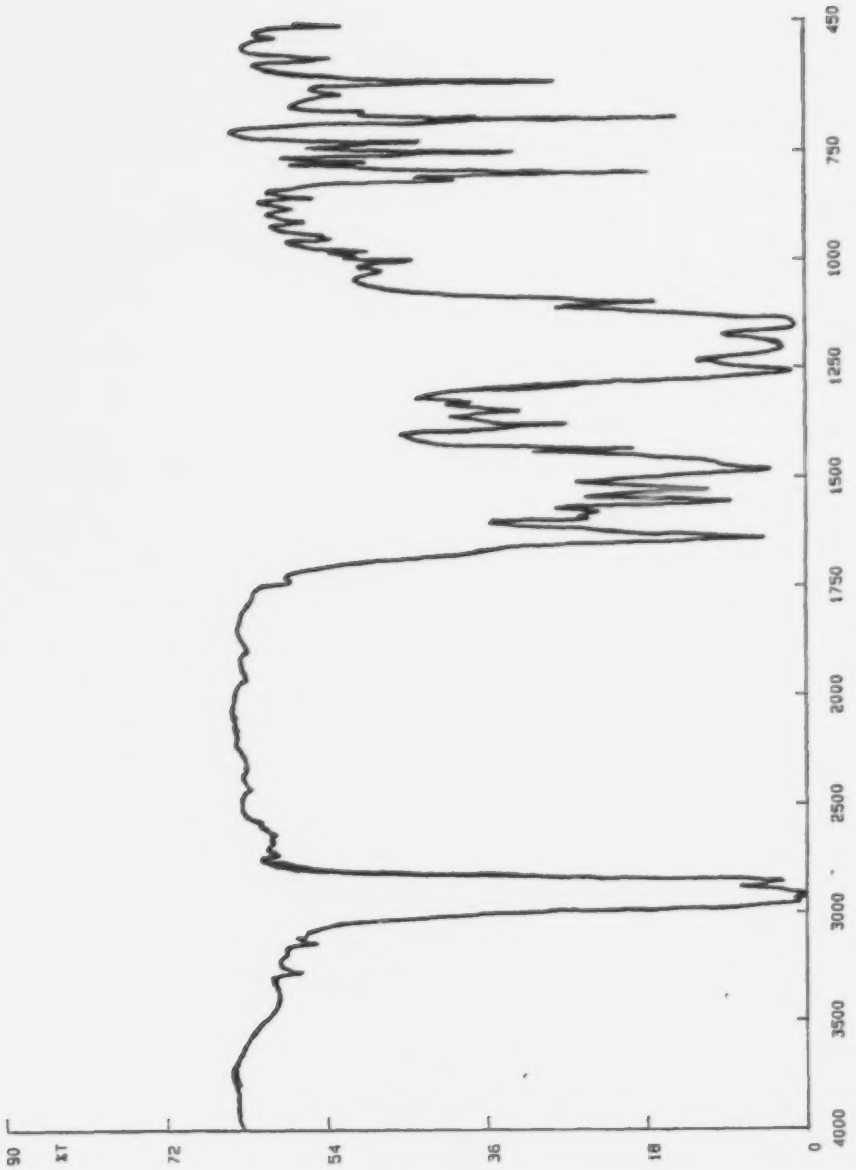


Figure 31: FTIR spectrum of Cu(hfac)·(1,5-COD) in nujol.

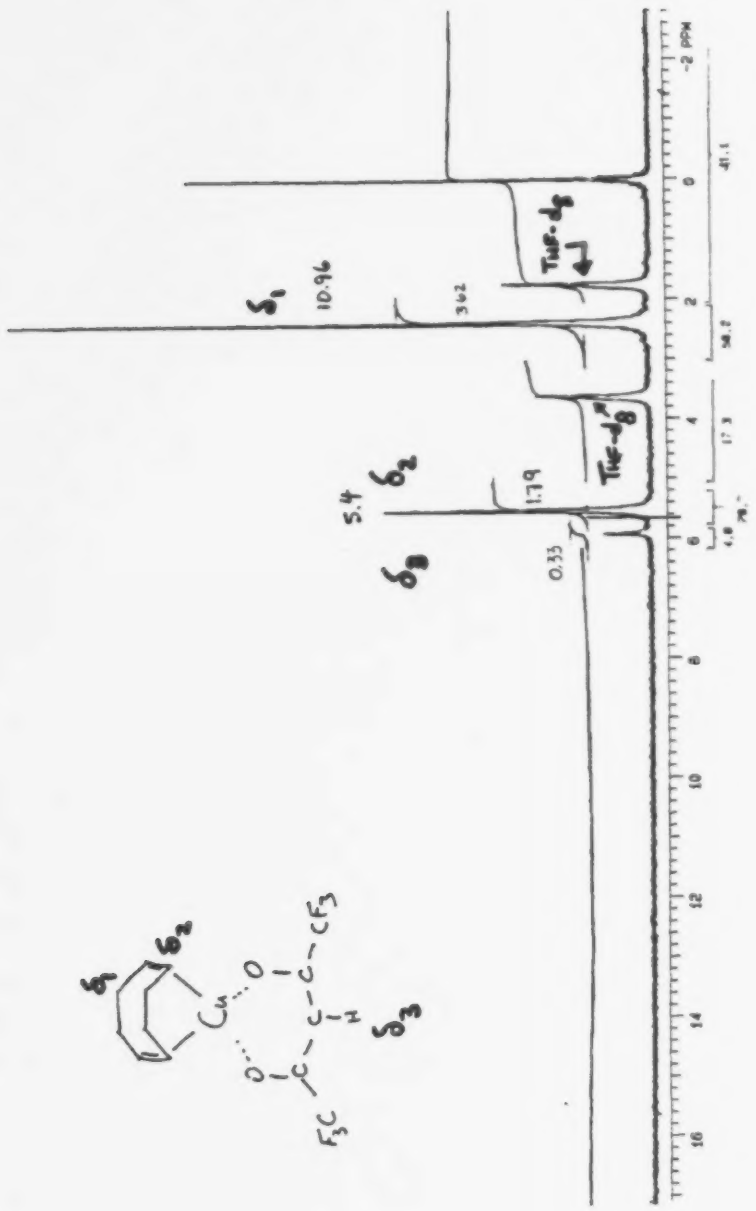


Figure 32: ^1H NMR spectrum of Cu(hfac)·(1,5-COD) in THF-d_8.

P143922.PDF [Page: 74 of 81]

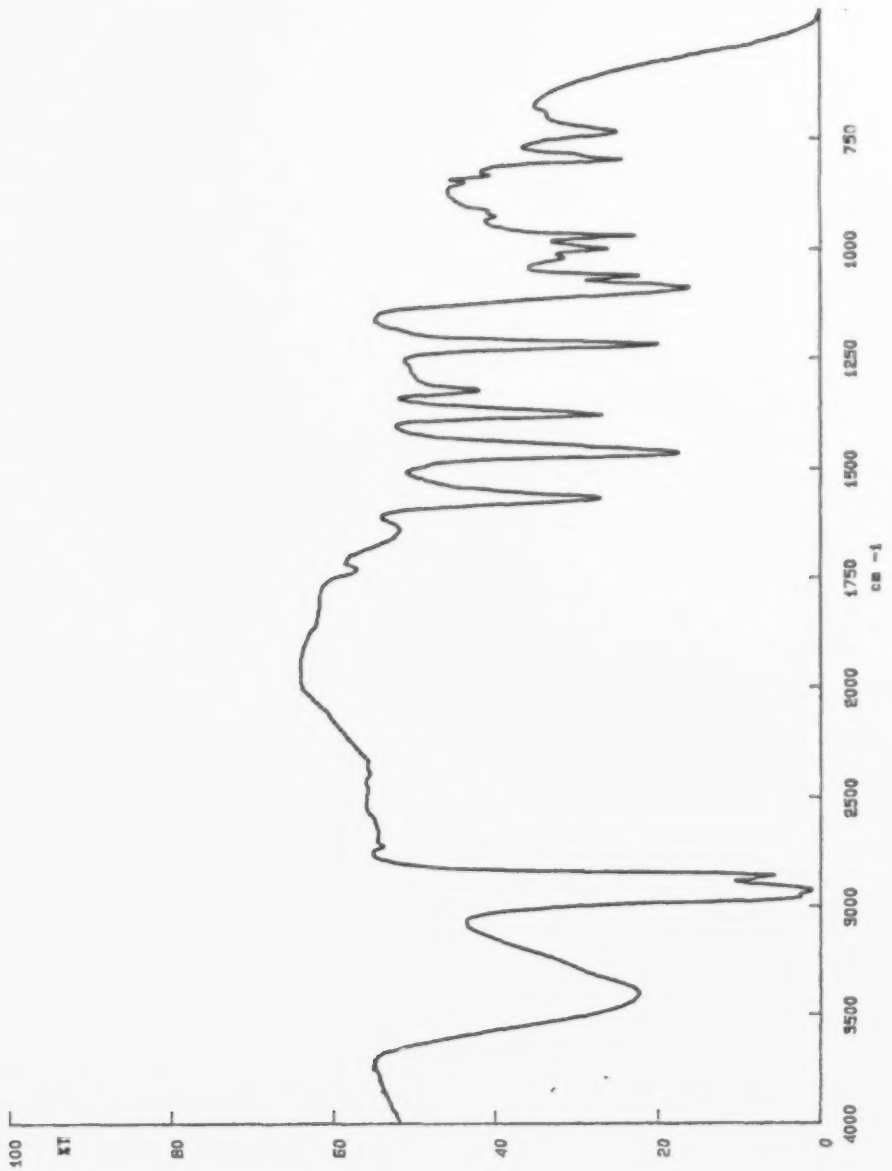


Figure 33: FTIR spectrum of $Cu(dmg)_2$'(TEDA) in nujol.

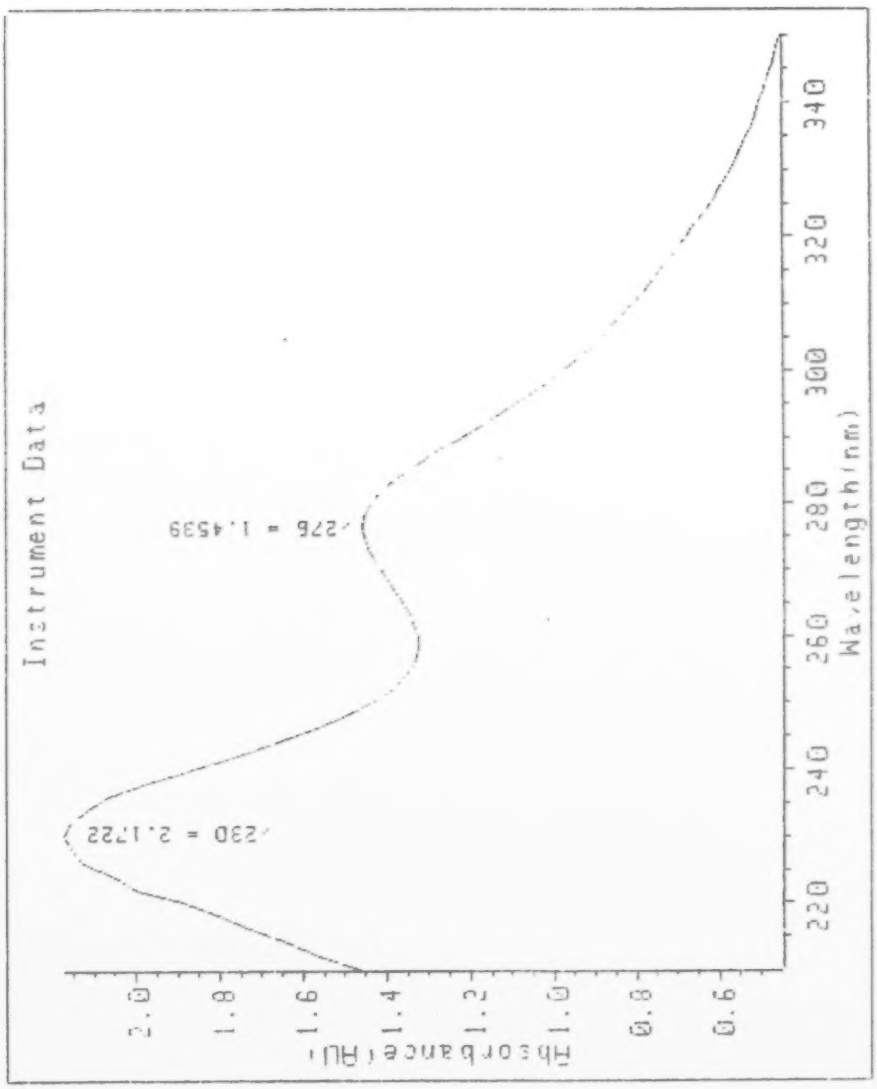


Figure 34: UV/VIS spectrum of $Cu(dmg)_2 \cdot (TEDA)$ in ethanol (2.9×10^{-4} M).

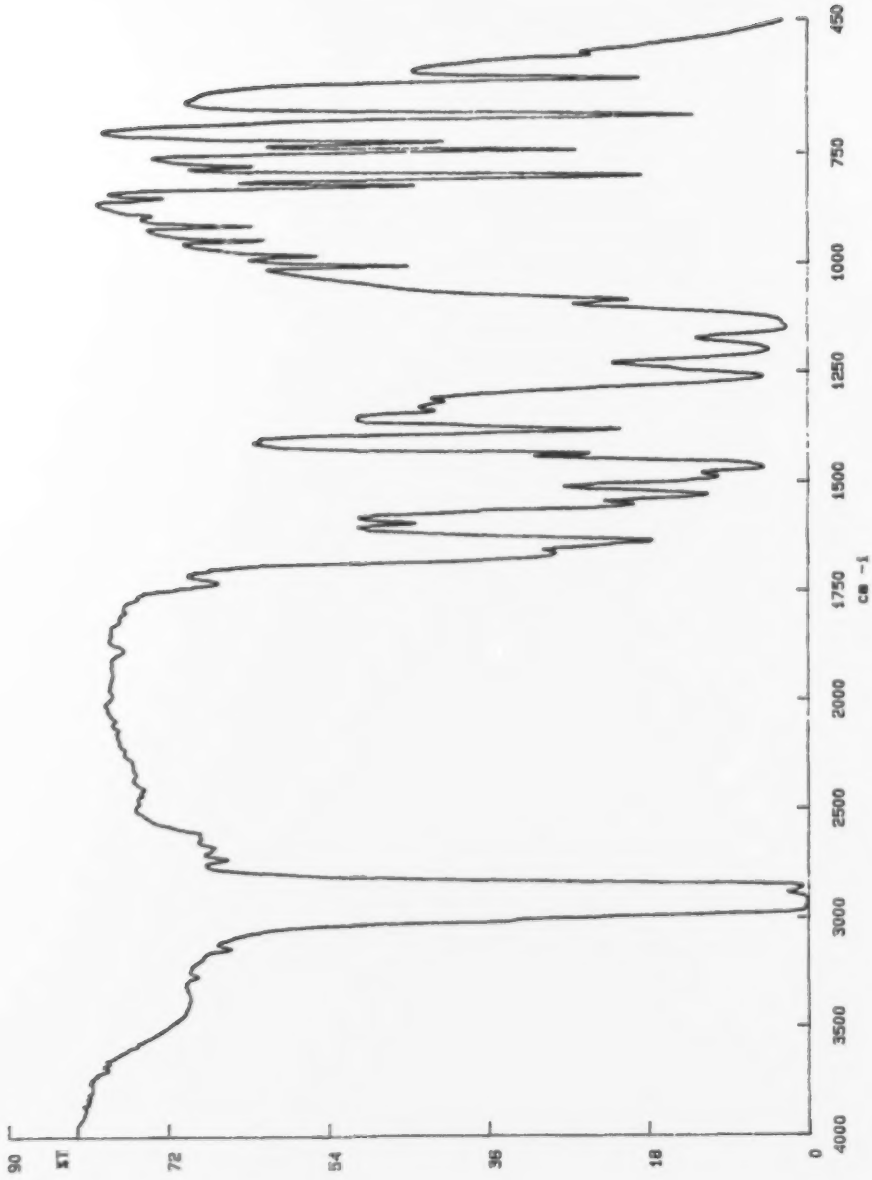


Figure 35: FTIR spectrum of Ag(hfac)·(1,5-COD) in nujol.

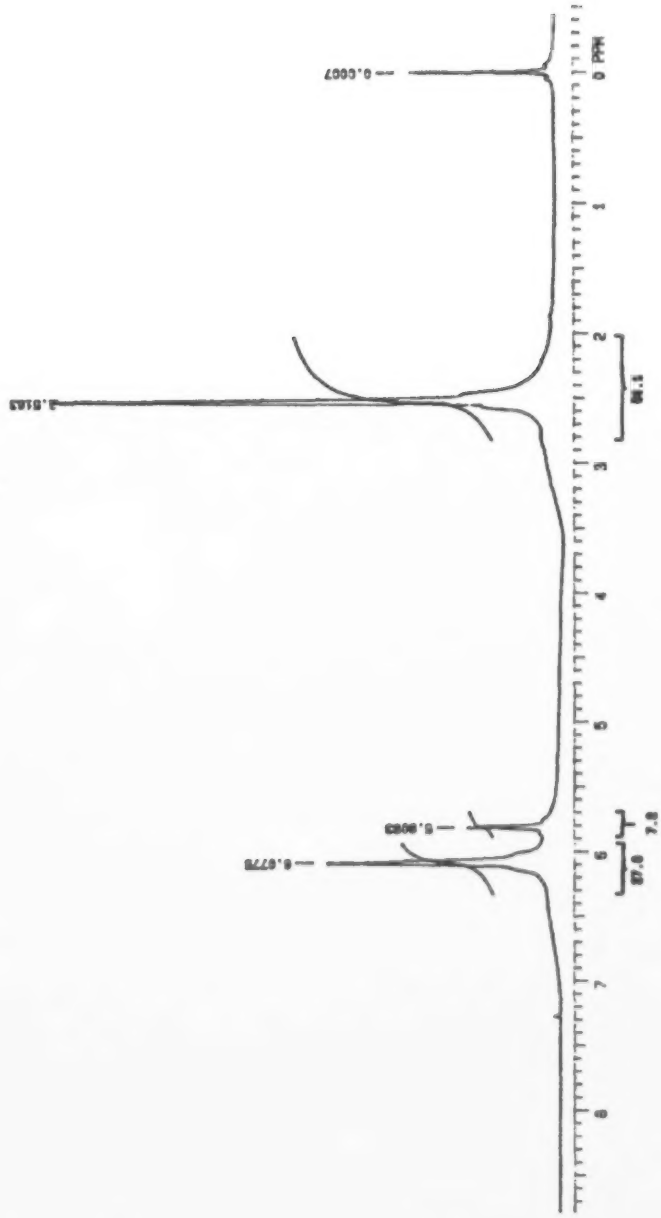


Figure 36: ^1H NMR spectrum of Ag(hfac)·(1,5-COD) in $CDCl_3$.

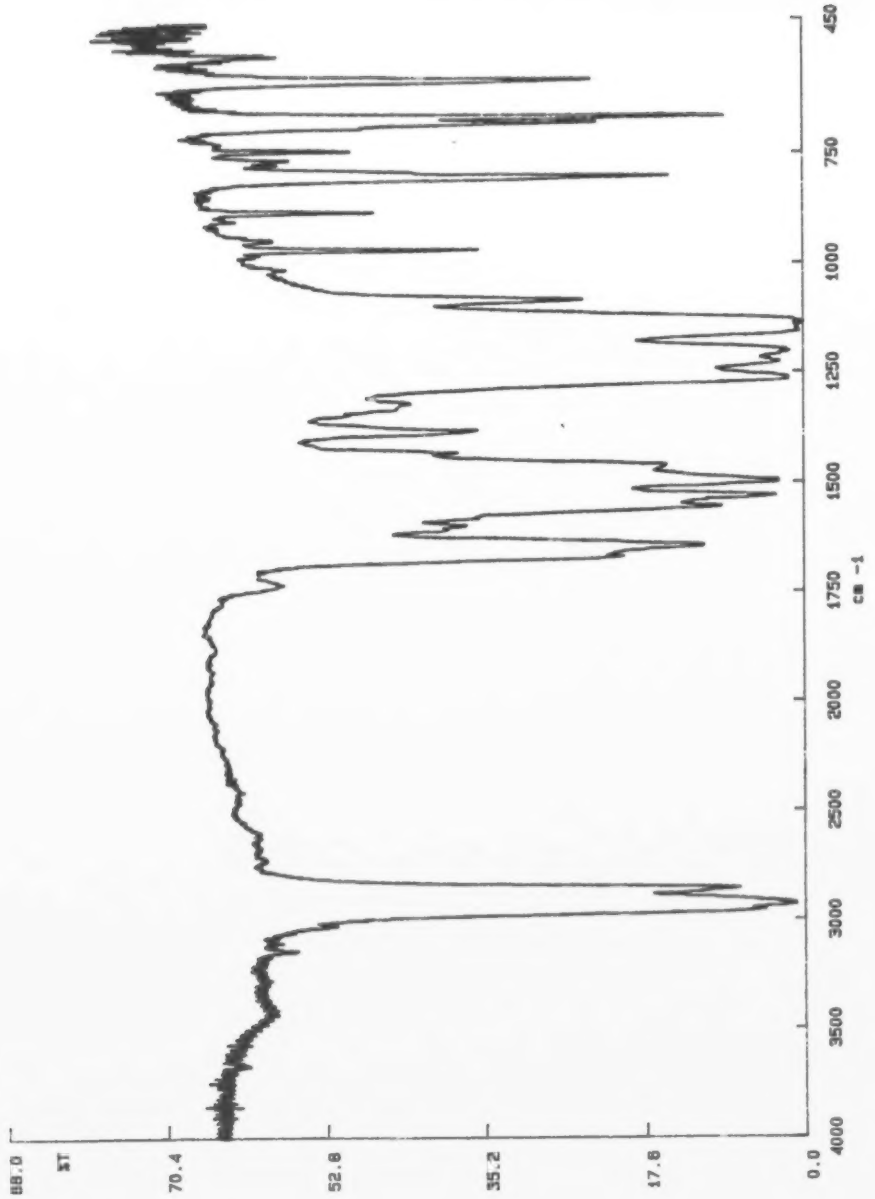


Figure 37: FTIR spectrum of Ag(hfac)·(1,4-CHD) in nujol.

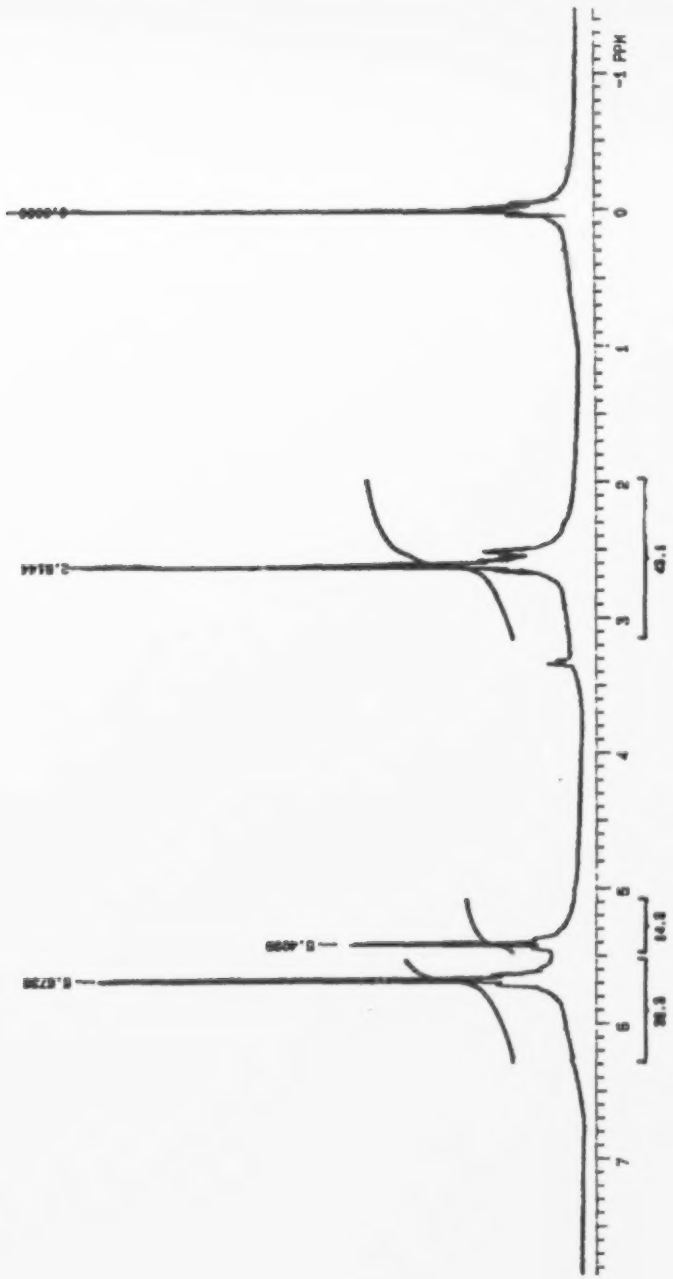


Figure 38: ^1H NMR spectrum of Ag(hfac)·(1,4-CHD) in DMSO-d_6.

P143922.PDF [Page: 80 of 81]

DOCUMENT CONTROL DATA

(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1. ORIGINATOR (the name and address of the organization preparing the document. Organizations for whom the document was prepared, e.g. Establishment sponsoring a contractor's report, or tasking agency, are entered in section 8.)

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
National Defence
Ottawa, Ontario, Canada K1A 0Z4

2. SECURITY CLASSIFICATION (overall security classification of the document including special warning terms if applicable)

UNCLASSIFIED

3. TITLE (the complete document title as indicated on the title page. Its classification should be indicated by the appropriate abbreviation (S,C or U) in parentheses after the title.)

NOVEL ACTIVATED CARBON IMPREGNANTS CONSISTING OF TRANSITION METAL COMPLEXES. PART I: BACKGROUND, SYNTHESES AND CHARACTERIZATIONS (U)

4. AUTHORS (Last name, first name, middle initial)

LIANG, Septimus H.C., WHALEN, J. Marc, COOPERSTOCK, Ramona L. and PATRICK, Brian O.

5. DATE OF PUBLICATION (month and year of publication of document)	6a. NO. OF PAGES (total containing information. Include Annexes, Appendices, etc.)	6b. NO. OF REFS (total cited in document)
JANUARY 1993	81	35

7. DESCRIPTIVE NOTES (the category of the document, e.g. technical report, technical note or memorandum. If appropriate, enter the type of report, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.)

REPORT

8. SPONSORING ACTIVITY (the name of the department project office or laboratory sponsoring the research and development. Include the address.)

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
National Defence
Ottawa, Ontario, Canada K1A 0Z4

9a. PROJECT OR GRANT NO. (if appropriate, the applicable research and development project or grant number under which the document was written. Please specify whether project or grant)	9b. CONTRACT NO. (if appropriate, the applicable number under which the document was written)
051LB	

10a. ORIGINATOR'S DOCUMENT NUMBER (the official document number by which the document is identified by the originating activity. This number must be unique to this document.)	10b. OTHER DOCUMENT NOS. (Any other numbers which may be assigned this document either by the originator or by the sponsor)
DREO REPORT 1197	

11. DOCUMENT AVAILABILITY (any limitations on further dissemination of the document, other than those imposed by security classification)

(X) Unlimited distribution
( ) Distribution limited to defence departments and defence contractors; further distribution only as approved
( ) Distribution limited to defence departments and Canadian defence contractors; further distribution only as approved
( ) Distribution limited to government departments and agencies; further distribution only as approved
( ) Distribution limited to defence departments; further distribution only as approved
( ) Other (please specify):

12. DOCUMENT ANNOUNCEMENT (any limitation to the bibliographic announcement of this document. This will normally correspond to the Document Availability (11). However, where further distribution (beyond the audience specified in 11) is possible, a wider announcement audience may be selected.)

P143922.PDF [Page: 81 of 81]

UNCLASSIFIED

SECURITY CLASSIFICATION OF FORM

13. ABSTRACT (a brief and factual summary of the document. It may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall begin with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (S), (C), or (U). It is not necessary to include here abstracts in both offical languages unless the text is bilingual).

// In the search for novel impregnants for activated carbon to enhance its chemical activity, a variety of organometallic complexes containing transition metals which may be used as impregnants have been synthesized. Copper, chromium, cobalt and silver are the transition metals employed. The ligands studied included triethylenediamine (TEDA), quinuclidine (QUIN), acetylacetonate (acac) and its fluoro-derivative, hexafluoro-acetylacetonate (hfac), and some cyclic dienes such as 1,5-cyclooctadiene (1,5-COD). In all, three classes of organometallic complexes were studied. The first class consisted of metal salts using TEDA (or QUIN) as ligands. The second class consisted of transition metals using acetylacetone, and TEDA (or QUIN) as ligands. The last class consisted of transition metals, using acetylacetonate and cyclic dienes as ligands. In this report, the synthetic routes and the characterization of these organometallic complexes obtained by various spectroscopic techniques are detailed. //

14. KEYWORDS, DESCRIPTORS or IDENTIFIERS (technically meaningful terms or short phrases that characterize a document and could be helpful in cataloguing the document. They should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location may also be included. If possible keywords should be selected from a published thesaurus. e.g. Thesaurus of Engineering and Scientific Terms (TEST) and that thesaurus-identified. If it is not possible to select indexing terms which are Unclassified, the classification of each should be indicated as with the title.)

IMPREGNANTS
ACTIVATED CARBON
TRANSITION METALS
ORGANOMETALLIC COMPLEXES
COPPER
CHROMIUM
COBALT
SILVER
TRIETHYLENEDIAMINE
FOURIER TRANSFORM INFRARED SPECTROSCOPY
ULTRA-VIOLET/VISIBLE SPECTROSCOPY
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY
ACETYLACETONE
HEXAFLUOROACETYLACETONE
1,5-CYCLOOCTADIENE
1,4-CYCLOHEXADIENE
1,3-CYCLOHEXADIENE
QUINUCLIDINE
SYNTHESES
CHARACTERIZATION

143922

94-04681

UNCLASSIFIED

SECURITY CLASSIFICATION OF FORM